REACTIONS OF FLUORINE AND BROMINE ATOMS.

By

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TO MY PARENTS AND JEAN.

ABSTRACT.

Hydrocarbons (chiefly the lower alkanes) have been fluorinated by a competitive method in a high vacuum, all glass, static system. Monofluorides formed by hydrogen abstraction from pairs of reactants have been measured by gas chromatography and ratios of A factors and activation energy differences found for reactions of the type,

$$F^{\bullet} + RH \longrightarrow HF + R^{\bullet} \qquad (2)$$

Absolute A factors for (2) have been obtained by assuming that the A factor for ethane calculated from transition-state theory was the same as the experimental A factor. Absolute activation energies for reaction (2) have also been obtained by assuming the activation energies for the higher of the alkanes investigated were zero.

Bromine hydrogen abstraction reactions analogous to (2) have been investigated by a similar method. Absolute A factors and activation energies have been derived by relating the results to the previously found parameters for bromine atom hydrogen abstraction from methyl bromide.

Previous work, both quantitative and qualitative, of bromine and fluorine atom hydrogen abstraction and related reactions has been described and the kinetic data summarised. The activation energies and A factors obtained here for bromine and fluorine atoms have been compared with previously found figures for chlorine. Good agreement has been found between experimental A factors and values calculated from transition-state theory.

From the bromine work carbon-hydrogen bond strengths have been derived which compare well with the generally accepted values. In order to obtain more accurate values a method has been developed for obtaining the activation energies of reactions of the type,

$$R^{\bullet} + HBr \longrightarrow RH + Br^{\bullet} \qquad (4)$$

Preliminary results are reported. Arrhenius parameters for other reactions in the bromine-hydrocarbon systems have been considered. Future work has been suggested.

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NOMENCLATURE AND UNITS.

Activation energies in the general text have been given the units kcal. The unit $mole^{-1}$ is understood. Logarithms of A factors have been given the units of the original numerical values.

Differentiation of isomeric hydrocarbons and alkyl halides is important in this work. A shorthand method has been used, e.g. t-BuBr represents tertiary butyl bromide. Bu can either denote "butyl" or "butane". Rate constants for hydrogen abstraction from a specific position in a molecule must also be differentiated. The system used is seen from an example: $k_{sn\text{-}Bu}$ is the rate constant for attack at secondary hydrogens in n-butane.

Round brackets can denote concentrations. Alkyl halides formed in the competitive method have been bracketed since they denote a measure of the final concentration of the halides.

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CHAPTER 1.

INTRODUCTION.

The reactions of halogen atoms may be divided into two main types.

1. Polar reactions in which one species donates and one accepts a pair of electrons to form a bond. When the bond is broken the electron pair remains with one of the fragments:

$$A{:}B \longrightarrow A{:} + B \qquad (1)$$

Examples of this type are found in the substitution of aromatic substrates at ordinary temperatures by chlorine, bromine and iodine[1]. Examples do also occur with aliphatic substrates, e.g. in the acid - and base - catalyzed halogenation of ketones where the halogen enters α to the carbonyl group.

2. Radical reactions in which species with odd electrons are involved:

$$A{:}B \longrightarrow A^{\cdot} + B^{\cdot} \qquad (2)$$

The exothermicity of halogen atom attack increases in the order F>Cl>Br>I and the tendency for radical reaction increases in the same order. Fluorine appears to react almost exclusively by this mechanism while iodine reacts with difficulty.

Free radical attack by halogen atoms on an organic substrate may be further divided into two main types depending on the substrate.

(a) Addition to a double bond in which the first step is the reaction,

$$X^{\cdot} + \rangle C = C\langle \longrightarrow \rangle \underset{X}{C} - \dot{C}\langle \qquad (3)$$

where $X^{\cdot}$ is a halogen atom.

(b) Substitution of the type,

$$X_2 + RY \longrightarrow RX + XY \qquad (4)$$

These reactions occur via the chain,

$$X\cdot + RY \longrightarrow YX + R\cdot \qquad (5)$$

$$R\cdot + X_2 \longrightarrow RX + X\cdot \qquad (6)$$

It is the kinetics of reactions of type (5), the rate determining step, that have been investigated in this work. X· in our case was either a bromine or fluorine atom and R an alkyl or halogen substituted alkyl group. In all cases Y was a hydrogen atom.

Chlorine reactions of this type have recently been investigated by a competitive method[2]. The present work is the extension of the same method to bromine and fluorine. Since a review of the work on chlorine has already been made[3], only the work on bromine and fluorine will be reviewed including some reference to the generation and handling of the latter. The experimental work on bromine and fluorine is treated separately, while the results, together with comparisons with chlorine, are discussed together.

CHAPTER 2

THE REACTIONS OF FLUORINE ATOMS.

2.1. INTRODUCTION.

Unfortunately very little work has been done on fluorine which leads to quantitative kinetic data on fluorine atom reactions with organic substrates. Workers have tended to investigate direct fluorination in order to develop methods of controlling the reaction and to prepare perfluorinated organic compounds. As a result too high fluorine:sample ratios have been used and the products obtained numerous and difficult to separate. A brief review of this type of work seems worth while, however, since it yields some qualitative information on the mode of fluorine attack, especially in view of the small amount of quantitative results that are available. Work previous to 1947 has been reviewed adequately by Bigelow[4,5]. Later cursory reviews have appeared[6,7,8].

The reaction of elementary fluorine on organic material is violent and complex. The former is well shown by the explosions of organic-fluorine mixtures encountered by the early workers. The effects were often exaggerated, however[9]. The work of Simons and Block[10] who obtained C_1 to C_7 perfluoro alkanes when fluorine and carbon were brought together in a metal tube in the presence of small amounts of mercury salts to prevent explosions, illustrates the latter. The complexity and violence may be explained by the thermochemistry of fluorine reaction with organics. Since the exothermicities of both fluorine addition (1) and substitution (2) attack at a carbon atom are in excess of 100 kcal.,

$$\begin{array}{l} -C \\ \| \\ -C \end{array} + F_2 \longrightarrow \begin{array}{l} -C\text{-}F \\ | \\ -C\text{-}F \end{array} \qquad (1)$$

$$H-\overset{|}{C}- + F_2 \longrightarrow -\overset{|}{C}-F + HF \qquad (2)$$

the energy released is greater than that required to break carbon-carbon bonds. As a result molecule smashing can and does occur.

2·2. QUALITATIVE DIRECT FLUORINATION.

Experimental methods were devised to control the fluorine activity. The method of Fredenhagen and Cadenbach[11] was developed by Bigelow and co-workers[12,13]. Reactions in the gas phase were carried out in brass vessels where fluorine, sometimes nitrogen diluted, and the organic sample were brought together from separate inlets. The gases were flowed either concurrently or countercurrently over a metal screen packing. This was usually copper wire perhaps with a coating of silver or other element. Its function was to break the reaction chains and to remove heat, although the fluorine coating which was present on the metal probably took part in the reaction.

In solution work fluorine was made to bubble through a sample stirred in a copper or nickel tube[14]. Reaction occurred probably at the gas liquid interface of bubbles. The inert requirements of solvents restricted the use of this method, although mild fluorinating conditions could be achieved as was shown by the first successful attempt to fluorinate a hydrocarbon by Bockemüller[15]. He obtained pure $C_6H_{11}F$ when fluorine diluted with CO_2 was bubbled through a dilute solution of cyclohexane in dichlorodifluoromethane contained in a glass apparatus at -80° C. The low solubility of organic compounds in liquid fluorocarbons also restricted the use of this method.

Direct fluorination of pure organic liquids could be carried out on relatively inert substrates with a low vapour pressure at the temperature of the experiment, e.g. the fluorination of chlorinated C_2 derivatives by Miller[14].

Very little solid phase work has been carried out.

Applications of Direct Fluorination Methods - Acids:- Bockemüller[15] bubbled diluted fluorine through a dilute solution of n-butyric acid in carbon tetrachloride at 0° C in a nickel reaction vessel. The products were

monofluoro butyric acids. n-Butyryl chloride and n-butyric acetic anhydride gave similar results. Isobutyric acid gave α-methyl -β- fluoropropionic acid. Halogen attack at the α-position to the active group in enolizable organic material is usually always ionic as is supported by the work of Kharasch and Brown[16]. They showed that when n-butyric acid is treated with an atomic reagent (SO_2Cl in the presence of benzoyl peroxide) β,γ-substitution occurred. Fluorine appears to react preferentially by an atomic mechanism, probably because the heterolytic cleavage of the molecule requires 100 kcal. more than the other halogens while the homolytic one does not differ essentially. The high electronegativity of the fluorine would account for this.

Aromatic Series:- Bockemüller also fluorinated benzoic acid in carbon tetrachloride solution in the presence of bromine to saturate intermediates during the reaction and so prevent dimerization. He obtained halogenated cyclohexanes by the addition of bromine and fluorine, e.g. $C_6H_6F_4Br_2$, showing the primary attack of fluorine on benzene is one of addition.

Work on the aromatic series was extended by Fukuhara and Bigelow[17] who fluorinated benzene in the gas phase over a copper packing in a heated vertical reaction vessel with nitrogen diluted fluorine in countercurrent flow. With ratios of fluorine:sample:nitrogen = 4:1:2, CF_4, C_2F_6, C_3F_8, C_5F_{10}, C_6F_{12}, C_6HF_{11} and $C_{12}H_{12}$ were obtained but no aromatic derivatives. Later work[18] was carried out on progressively more and more deactivated fluoro aromatic compounds with a typical mixture fluorine:sample:nitrogen = 3:1:12. Copper sheet was used as a packing in a heated reaction vessel. No aromatic products were obtained. It was concluded that all these results were in accordance with the

assumption that the first step was the addition of fluorine to the benzene ring, destroying its aromatic character. The ring behaved subsequently as a substituted cyclohexadiene and as such might undergo:

(1) addition of fluorine (2) substitution of fluorine

(3) addition of HF (4) polymerization (5) fragmentation, either concurrently or successively.

Attempts have been made to explain the absence of aromatic fluorine derivatives and the fracturing of the molecules on thermochemical grounds. The high values of the heats of reaction of the fluorination of aromatic compounds compared with other halogenations are shown below.

	X = F	Cl	Br
$C_6H_6 + X_2 \longrightarrow C_6H_5X + HX +$	103.5	23.9	7.7 kcal.
$\frac{1}{3}C_6H_6 + X_2 \longrightarrow \frac{1}{3}C_6H_6X_6 +$	95.7	23.9	7.1 kcal.

Enough energy would be released in fluorination to break carbon-carbon bonds since D(C-C) $<$ 90 kcal. Addition would be slightly favoured. However Pavlath[19] has pointed out that halogenation of aromatic compounds through a radical reaction mechanism will result in addition except at high temperatures. The halogen substitution of an aromatic system generally requires an electrophilic reaction mechanism. Since fluorine favours a radical mechanism, addition will dominate.

Acetone:- Fukuhara and Bigelow[20] fluorinated acetone by a method similar to benzene. The products identified were CF_4, COF_2, CF_3COF, $CF_3CO.CF_3$ (main), $(COF)_2$ and $CH_2F.CO.CH_3$. Bigelow[5] has suggested the following mechanism:

$$CH_3CO.CH_3 \longrightarrow CF_3CO.CF_3 \text{ by successive substitution} \qquad (3)$$

$$CF_3CO.CF_3 + F\cdot \longrightarrow CF_3CO\cdot + CF_4 \qquad (4)$$

$$CF_3CO\cdot + F_2 \longrightarrow CF_3COF + F\cdot \quad (5)$$

$$CF_3COF + F\cdot \longrightarrow CF_4 + \cdot COF \quad (6)$$

$$\cdot COF + F_2 \longrightarrow COF_2 + F\cdot \quad (7)$$

$$2\cdot COF \longrightarrow O{=}\underset{F}{\overset{|}{C}}{-}\underset{F}{\overset{|}{C}}{=}O \quad (8)$$

Here it is seen that fragmentation products instead of polymerization have become important.

Chlorohydrocarbons:- The fluorination of halogen substituted hydrocarbons has been studied extensively. When Bockemüller[15] bubbled diluted fluorine through tetrachloroethylene in difluorodichloromethane solution at -80° C he obtained not only the expected $CFCl_2CFCl_2$ but also CCl_3CFCl_2 and $C_4F_2Cl_8$, indicating the formation of a chlorinating agent during the reaction probably by fluorine attack on the solvent.

Bigelow et alia[21] found a similar effect in their study of the vapour phase screen fluorination of ethyl chloride. Among the products were CF_4, CF_3Cl, CF_3CF_2Cl, CHF_2CH_2Cl and $CF_2 = CCl_2$, indicating substitution by both fluorine and chlorine. Fragmentation had also occurred as well as unsaturation.

Miller[14] investigated the fluorination of saturated and unsaturated chlorohydrocarbons in the liquid phase. He was the first to react fluorine successfully with pure liquid organic compounds containing more than one carbon atom. The fluorine and pure liquid sample or a solution in CF_3CCl_3 were caused to move in countercurrent flow in a temperature controlled (0-90° C) metal apparatus.

The products from pure pentachlorethane at 90° C were $CFCl_2CFCl_2$(2%) $CCl_2{=}CCl_2$(7%), CCl_3CFCl_2(30%), C_2Cl_6(9%) and C_4Cl_{10}(trace). The presence of olefin might be explained by chlorine atom dissociation from the intermediate $C_2Cl_5\cdot$ radical rather than the mechanism proposed by Bigelow[5] which was:

$$CCl_3CHCl_2 + F\cdot \longrightarrow HF + CCl_3CCl_2\cdot \quad (9)$$

$$CCl_3CCl_2\cdot + F_2 \longrightarrow ClF + CCl_2{=}CCl_2 + F\cdot \quad (10)$$

$$CCl_3CCl_2\cdot + ClF \longrightarrow CCl_3CCl_3 + F\cdot \quad (11)$$

$$2CCl_3CCl_2\cdot \longrightarrow CCl_3CCl_2CCl_2CCl_3 \quad (12)$$

$$CCl_2{=}CCl_2 + F_2 \longrightarrow CFCl_2CFCl_2 \quad (13)$$

He suggested[4] ClF as the chlorinating agent in these types of reaction, for hydrogen substitution at least, because of the high heat of formation of HF. It would readily be formed by,

$$RCl + F\cdot \longrightarrow ClF + R\cdot \quad (14)$$

However he does not deny the possibility of,

$$RCl + F\cdot \longrightarrow RF + Cl\cdot \quad (15)$$

or even,

$$R_2C{=}CR_2 + FCl \longrightarrow R_2CF.CR_2\cdot + Cl\cdot \quad (16)$$

producing atomic chlorine. The formation of $CHFCl.CCl_3$ and $CHCl_2CFCl_2$ but no $CCl_2{=}CCl_2$ in a similar fluorination of $CHCl{=}CCl_2$ at 0° C by Miller[14] would favour ClF as the agent.

With tetrachloroethylene at 0° C the products were $CFCl_2CFCl_2$(12%), CCl_3CFCl_2(11%) and $CFCl_2CCl_2$-CCl_2CFCl_2(18%). Walling[6] has suggested that the dimer arises from the reaction,

$$2CFCl_2CCl_2\cdot \longrightarrow CFCl_2CCl_2CCl_2CFCl_2 \quad (17)$$

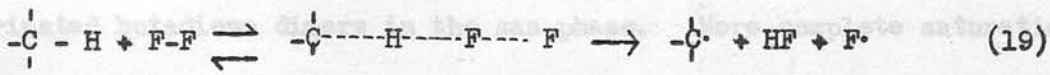
The very large amount of dimer present would then indicate that the kinetic chains were very short. Rapid chain initiation must have been required to maintain the high radical concentration necessary for the very fast reaction which certainly occurred.

Miller[22,23] and his co-workers have suggested that since fluorination occurs equally well at -80° C as at room temperature, chains would have to be exceedingly long if

$$F_2 \longrightarrow 2F\cdot$$

were the only initiation step. Because of the indication to the contrary suggested by dimer formation they have suggested that (18), (19) could initiate chains at temperatures below 100° C.

(18)

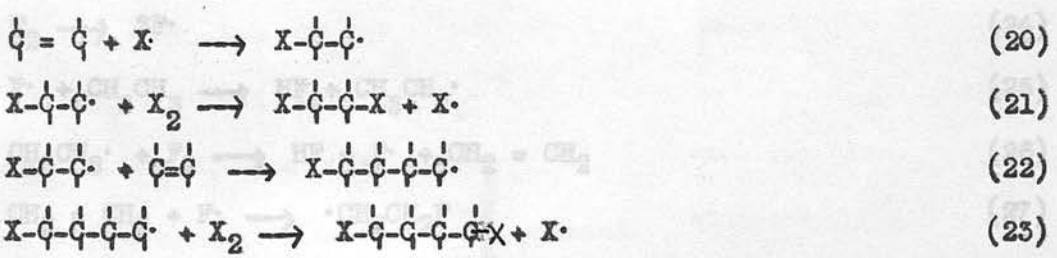


(19)

ΔH for ethylene and methane would be ~ -2 keal. and 2 keal respectively.

As proof of this mechanism they have cited the promotion by small amounts of fluorine of the oxidation of tri - and tetrachlorethylene at 0 to -15° C. Fluorine also promotes chlorination, as was shown by McBee[24] who chlorinated hexane by dissolving it in liquid chlorine and passing fluorine through the solution.

It should be pointed out however that if, instead of the dimer occurring by radical recombination as is claimed by Miller, the following reactions took place in the case of olefins[5]:



(20)

(21)

(22)

(23)

where X = F or Cl and X_2 = ClF or F_2 or Cl_2

then dimer could be formed without breaking the chain. It is also significant that dimer formation is often only excessive in the case of olefins, e.g. in liquid phase work[14] $CCl_2 = CCl_2$ gave $CFCl_2CCl_2CCl_2CFCl_2$ in large yield while $CHCl_2CHCl_2$ yielded largely CCl_3CFCl_2. These facts would contradict the occurrence of short chains and Miller's initiation reactions would not be required.

Atomic fluorine could account for the promotion effect provided the chains initiated were not too short, despite the low equilibrium constant for fluorine dissociation ($2{\cdot}9 \times 10^{-21}$ at 25°C).

In a later paper Miller[25] investigated the fluorination of halogeno-mono-olefins and halogeno-butadiene dimers in the liquid phase and completely fluorinated butadiene dimers in the gas phase. More complete saturation of the olefins occurred in the gas phase.

Alkanes:- The work of Bigelow and co-workers in the gas phase leads to a possible mechanism for the fluorination of alkanes. In the study of the fluorination of ethane[12,26] by the copper screen method with typical fluorine: sample:nitrogen ratios of 4:1:12 the products were CF_4, C_2F_6, CF_3CHF_2, CHF_2CHF_2 and CHF_2CH_2F; but no di - or monofluoroethanes. When the ratios were 1:1:12, very little CF_4 and no C_2F_6 were formed. In view of the absence of the lower fluorides, Bigelow[4] has suggested the following mechanism. Fluorine atoms were assumed to be generated thermally or catalytically.

$$F_2 \longrightarrow 2F\cdot \qquad (24)$$

$$F\cdot + CH_3CH_3 \longrightarrow HF + CH_3CH_2\cdot \qquad (25)$$

$$CH_3CH_2\cdot + F_2 \longrightarrow HF + F\cdot + CH_2 = CH_2 \qquad (26)$$

$$CH_2 = CH_2 + F\cdot \longrightarrow \cdot CH_2CH_2F \qquad (27)$$

or a combination of

$$CH_3CH_2\cdot + F_2 \longrightarrow HF + \cdot CH_2CH_2F \qquad (28)$$

$$\cdot CH_2CH_2F + F_2 \longrightarrow HF + CH_2FCHF\cdot \qquad (29)$$

$$CH_2FCHF\cdot + F_2 \longrightarrow F + CH_2FCHF_2 \text{ (product)} \qquad (30)$$

$$CH_2FCHF_2 + F\cdot \longrightarrow HF + \cdot CHFCHF_2 \qquad (31)$$

$$\cdot CHFCHF_2 + F_2 \longrightarrow F\cdot + CHF_2CHF_2 \text{ (product)} \qquad (32)$$

and so on until hexafluoroethane was reached and ultimately cleaved to carbon tetrafluoride. Direct successive substitution probably could also have occurred with other mechanisms since more unidentified products were formed. This demonstrates the cleavage of hydrocarbons by fluorine.

Hadley and Bigelow[27] studied the fluorination of methane under the same conditions. The reaction proved to be more complex since not only CF_4, CHF_3, CH_2F_2 and CH_3F were formed but also C_2F_6 and C_3F_8, demonstrating the carbon chain may be built up as well as broken down. The mechanism here might be;

$$CH_4 + F\cdot \longrightarrow CH_3\cdot + HF \qquad (33)$$

$$CH_3\cdot + F_2 \longrightarrow CH_3F + F\cdot \qquad (34)$$

and so on until CF_4 is formed. At the stage,

$$F\cdot + CHF_3 \longrightarrow HF + CF_3\cdot \qquad (35)$$

the highly fluorinated radical does not react so readily with fluorine molecules and (36) might occur:

$$2CF_3\cdot \longrightarrow C_2F_6 \qquad (36)$$

also $$F\cdot + CH_2F_2 \longrightarrow HF + \cdot CHF_2 \qquad (37)$$

$$CF_3\cdot + \cdot CHF_2 \longrightarrow CF_3CHF_2 \qquad (38)$$

$$CF_3CHF_2 + F\cdot \longrightarrow HF + CF_3CF_2\cdot \qquad (39)$$

$$CF_3\cdot + CF_3CF_2\cdot \longrightarrow C_3F_8 \qquad (40)$$

Higher polymers might also have been present.

With the advent of World War II workers tried to make direct fluorination efficient in the preparation of fluorocarbons by the use of higher temperatures, higher fluorine to sample ratios and coated copper packings[28,29,30]. Bigelow, continuing his search for more controlled conditions despite general opinion that direct fluorination would never be an economic proposition, developed a jet fluorination reactor[31]. A highly turbulent jet of the diluted organic reactant was mixed with fluorine. Ethane gave a high yield of perfluoroethane

with very little cleavage or polymerization using the ratios fluorine:sample: nitrogen = 6:1:12.

Nitrogen-Containing Compounds:- Later papers on the direct fluorination in the gas phase showed the reaction of fluorine on nitrogen containing compounds is very complex. CF_4, C_2F_6, CF_3NF_2, $CF_3CF_2NF_2$ and $(CF_3)_2NF$ were reported, for example, from the fluorination of CH_3NH_2 in the gas phase[32]. Work on malononitrile and dimethylformamide shows that since C_2F_6 and CF_3NF_2 were absent fluorinolysis and cyclisation could take place before the reaction had reached the perfluorinated state.

Summary of Qualitative Results:-

(1) Fluorination occurs almost exclusively by a radical mechanism even in the aromatic series.

(2) The mechanism of attack with high fluorine:sample ratios may be[5]:

$F_2 \rightleftharpoons 2F^{\bullet}$ (24) thermally, catalytically or both after which addition,

$$R_2C = CR_2 + F^{\bullet} \longrightarrow R_2CF.CR_2^{\bullet} \qquad (41)$$

$$R_2CF.CR_2^{\bullet} + F_2 \longrightarrow R_2CF.CFR_2 + F^{\bullet} \qquad (42)$$ and so on

or substitution,

$$RH + F^{\bullet} \longrightarrow HF + R^{\bullet} \qquad (43)$$

or, $$RX + F^{\bullet} \longrightarrow XF + R^{\bullet} \qquad (44)$$

$$R^{\bullet} + F_2 \longrightarrow RF + F^{\bullet} \qquad (45)$$ and so on

Reactions (24), (41), (43) and (44) may be replaced by (18) and (19) at lower temperatures;

or fragmentation,

$$RCF_2CF_2R + F^{\bullet} \longrightarrow RCF_3 + {}^{\bullet}CF_2R \qquad (46)$$

$${}^{\bullet}CF_2R + F_2 \longrightarrow RCF_3 + F^{\bullet} \qquad (47)$$ and so on

or dimerization,

$$R^{\bullet} + R^{\bullet} \longrightarrow R.R \text{ (chain broken)} \qquad (48)$$

and finally polymerization. The radical formed by the addition of a fluorine atom to a double bond may react with another unsaturated molecule;

$$R_2CF.CR_2^{\bullet} + R_2C = CR_2 \longrightarrow R_2CF.CR_2CR_2CR_2^{\bullet} \qquad (49)$$

and so on until

$$R_2CF.(CR_2)_nCR_2^{\bullet} + F_2 \longrightarrow R_2CF.(CR_2)_nCFR_2 + F^{\bullet} \qquad (50)$$

$R^{\bullet}$ may represent the same or different alkyl groups completely fluorinated or not and $X^{\bullet}$ denotes $Cl^{\bullet}$ or $Br^{\bullet}$. Also head-to-head and tail-to-tail type polymerization might occur, as well as branched chains or combinations of conjugated systems and many chain-breaking steps. This mechanism is by no means proven. From our results olefin formation could well be an important intermediate step in the attack of saturated substrates.

(3) Fragmentation or polymerization may be favoured according to the case in question.

(4) Chlorination of compounds already containing chlorine or in the presence of a chlorine-containing solvent can occur along with fluorination.

(5) The first step in the fluorination of the aromatic series is the addition of a fluorine atom.

(6) It is sometimes possible for fluorinolysis and cyclisation to occur before the perfluorinated stage is reached.

(7) Unsaturation of a previously saturated substrate can sometimes occur.

2·3. QUANTITATIVE WORK.

Tedder developed a method of carrying out controlled fluorinations of liquid organic compounds at low temperatures. Following a report of the formation of monofluoro derivatives from n-hexane, propionyl fluoride and methyl ethyl ketone in a preliminary paper[34] later work gave semi-quantitative information on fluorine attack of liquid hydrocarbons.

Anson and Tedder[35] studied the liquid phase fluorination of n-butane between -33 and -101° C and isobutane at -80° C. A mixture with fluorine: nitrogen = 1:4 was bubbled through the liquid hydrocarbons in a pyrex vessel to give 15% fluorination. The ratios of n-butyl fluoride / s-butyl fluoride and isobutyl fluoride / t-butyl fluoride were measured at each temperature by gas chromatography. Each type of hydrogen present on the molecules was attacked in the order tertiary > secondary > primary. Fluorination was temperature independent but this was thought to be due to the gas phase reaction occurring in bubbles at a temperature much higher than that recorded. However an examination of the mean ratios found shows the result n-BuF/s-BuF = 1·26:1 is almost identical with that found in our work(1·30). Also the result i-BuF/t-BuF = 4.01:1 is lower than our result (6.4). Now since it is the primary position that would show any activation energy more readily, if their reaction was occurring at temperatures higher than recorded the primary would increase in amount and so raise the ratio. This most certainly has not happened and would indicate that the fluorination was temperature independent. It is interesting that the activation energy for the similar chlorination of n-butane was only slightly higher than that found later in the gas phase. It should be noted that molecular ratios have been quoted here.

Subsequently n-butane and isobutane were fluorinated, chlorinated and brominated in the gas phase[36]. In the fluorination two preheated gas streams

of nitrogen/hydrocarbon and nitrogen/fluorine were mixed and flowed at 180cc/min through either a glass or copper reaction vessel. The ratios of hydrocarbon:fluorine:nitrogen were 5:0·75:80. n-Butane was studied at 25 and 125° C and reliable results were obtained only at 25° C for isobutane. The ratios of s-butyl fluoride / n-butyl fluoride and t-butyl fluoride / isobutyl fluoride were measured by gas chromatography.

From the competitive method[37] this work gave the ratios of rate constants for the hydrogen abstraction by a fluorine atom at the secondary and primary positions in n-butane and tertiary and primary in isobutane. After making allowance for the number of hydrogens of each type present the results obtained were:

$$k_{sn\text{-}Bu}/k_{pn\text{-}Bu} = 1{\cdot}1 \exp(97 \pm 20/RT);$$

and $$k_{ti\text{-}Bu}/k_{pi\text{-}Bu} = 1{\cdot}39 \pm 0{\cdot}16 \text{ at } 298^{\circ} \text{ K}.$$

Chlorination of the hydrocarbons was carried out similarly. No preheating was necessary but illumination was required to give reaction. It is interesting to compare the results with those obtained by the static-method of Knox and Nelson[2]. The ratios were:

$$k_{sn\text{-}Bu}/k_{pn\text{-}Bu} = 1{\cdot}8 \exp(480 \pm 70/RT) \text{ - Anson, Fredricks and Tedder}$$
$$= 1{\cdot}6 \exp(520/RT) \text{ - Knox and Nelson}$$

and $$k_{ti\text{-}Bu}/k_{pi\text{-}Bu} = 2{\cdot}1 \exp(540 \pm 70/RT) \text{ - Anson, Fredricks and Tedder}$$
$$= 1{\cdot}3 \exp(800/RT) \text{ - Knox and Nelson}$$

There are slight differences in the latter results. Of the two, however, those of Knox and Nelson appear suspect since the internal energy of activation derived on an absolute scale for the tertiary attack is negative to the extent of 500 cal. For a flow method Tedder's results are remarkably good, although the accuracy to show an activation energy for fluorine cannot be claimed.

Bromination was also carried out by introducing bromine into the gas stream from a constant temperature trap through which nitrogen was bubbled. n-Butane was investigated only at 146° C because of product decomposition and too high selectivity at higher and lower temperatures. The reaction mixture was n-butane:bromine:nitrogen = 5:0·5-1:80. Because of its extreme reactivity the tertiary in isobutane could only be competed with the secondary in n-butane at 160° C using the ratios n-butane:isobutane:bromine:nitrogen = 3:3:1:120.

As with fluorine these investigations lead to the ratios of rate constants per hydrogen type:

$k_{sn\text{-}Bu}/k_{pn\text{-}Bu} = 82 \pm 15$ at 419° K

$k_{ti\text{-}Bu}/k_{pi\text{-}Bu} = 1{,}640 \pm 300$ at 433° K.

The latter result was obtained from $k_{pi\text{-}Bu}/k_{sn\text{-}Bu}$ on the assumption that the primary in isobutane was similar to that in n-butane.

In a recent paper Fredricks and Tedder[38] fluorinated, chlorinated and brominated the n-butyl halides in the gas phase by the same method as before. All possible monohalogenated products from attack at C_1-C_4 were analysed for, by gas chromatography where possible. By taking into account the number of hydrogens at each position the relative rates of attack at each carbon was found for the individual halides relative to the attack at C_4 which was taken as unity.

n-Butyl fluoride and chloride were fluorinated at 20° C. In the fluoride case 1,1- difluorobutane was analysed by mass spectrometry and the results used in conjunction with the 1,2- and 1,4- isomers found by gas chromatography. The 1-chloro-2-fluoro and 1-chloro-3-fluoro derivatives could not be separated in the fluorination of the chloride.

n-Butyl fluoride, chloride and bromide were brominated at 146° C. No 4-bromo product could be found with the chloride and fluoride. Since the relative attack at carbon 3 found in the previous paper was 82 for n-butane it was assumed

to be the same for the fluoro and chloro butanes. This assumption was supported by the competitive chlorination of n-butane and n-butyl chloride. The ratios of 2-chlorobutane and 1,3-dichlorobutane were virtually unity, showing the 3-positions behaved similarly. This result combined with the similarity in the relative rates for C_3 attack in all cases showed the rate of attack at C_4 was almost always identical for these cases.

Data about bromine substitution β to a bromine atom was difficult to obtain. Compared with the corresponding chloride and fluoride n-butyl bromide reacted only very slowly. The only product in any amount was 1,3- dibromobutane. This was thought to be due to the instability of the intermediate radical:

$$CH_2BrCHCH_2CH_3\cdot \longrightarrow Br\cdot + CH_2 = CHCH_2CH_3 \qquad (51)$$

A similar effect was reported by Rust and Vaughan[39] who found in the region of 200° C the rate of chlorination at the βcarbon atom to the chlorine in n-butyl chloride decreased with increasing temperature. Ash and Brown[40] suggested this "vicinal" effect was due to the instability of the intermediate $CH_2ClCHC_2H_5\cdot$ radical. In Tedder's case with the corresponding bromo-butyl radicals, 1,2-dichloro-butane was found in place of the expected 1-bromo-2-chloro product at 37 and 78° C in the chlorination of n-butyl bromide. Slight decomposition of the chloro-butyl radical in the chlorination of n-butyl chloride occurred at 146° C.

A summary of the results are given below. All the figures quoted are the relative rates of attack per hydrogen at the positions indicated.

Fluorination

Temp° C	X	CH_2X	CH_2	CH_2	CH_3
20	H	1	1·3	1·3	1
20	F	<0·3	0·8	1·0	1
21	Cl	?	1·7		1

Bromination

Temp° C	X	CH_2X	CH_2	CH_2	CH_3
146	H	1	82	82	1
146	F	10	9	82	1
146	Cl	34	32	82	1

Chlorination

146	H	1	3·3	3·3	1
146	F	0·9	1·6	3·2	1
146	Cl	0·7	1·6	3·4	1
78	Br	0·4	-	3·6	1

The over-all effects on halogenations by a halogen already present in the n-butane molecule were:

(1) F>Cl>(Br) in the retardation of substitution at the β-atom.

(2) Fluorine slightly deactiviated the γ-position.

(3) Substitution at the α-carbon atom also affected but strongly dependent on the attacking radical.

The difference in behaviour of the attacking radicals were:

(4) The selectivity was in the order Br>> Cl > F.

(5) At the β-carbon atom bromination was relatively the least affected by the halogen already present and fluorination the most.

(6) At the α-carbon atom fluorination appeared to be appreciably, and chlorination slightly, retarded by the substituent halogens in the order Br > Cl ≃ F, but bromination was activated.

These rules may hold for the halides of ethane and higher hydrocarbons. Methane may be an exception in the case of fluorination and chlorination. Methyl chloride[41,42] chlorinates faster than methane and there is some indication that methyl fluoride[43] fluorinates faster than the parent hydrocarbon also (see below).

One paper is closely allied to this work. Mercer and Pritchard[43] competed hydrogen and methane mixtures with gaseous fluorine over the temperature range 25-150° C in both inconel and quartz reaction vessels. Reaction was followed by the consumption of reactants. Fluorine generated in situ was compressed into the reaction system. A typical mixture was $F_2:H_2:CH_4$: inert = 1:3:3:350. The thermal reaction appeared to give C_2F_6 heterogeneously in the metal vessel, while a medium pressure mercury lamp was required to give mainly 65% CH_3F and 30% CH_2F_2 (this ratio indicating perhaps that methyl fluoride fluorinates faster than methane). Thermal reaction did not occur between hydrogen and fluorine until 100° C. In the quartz vessel, however, above 18° C reaction proceeded spontaneously but slowly. Because of the necessity for illumination in the metal vessel and the independence of the relative rate constants on large variations in reactant pressures and consumption, the reaction

$$CH_4 + F_2 \longrightarrow CH_2\cdot + 2HF \qquad (52)$$

was discounted in favour of atomic initiation. The result obtained was

$$k_{Me}/k_{H_2} = 1{\cdot}05 \exp (0{\cdot}5 \pm 0\ 2/RT).$$

While the importance of the type of wall surface cannot be denied[44], the purity of the fluorine sample which varies from cell to cell must also be considered, especially when slow reaction occurs.

Although the evidence for reactions of the type,

$$Y + F_2 \longrightarrow YF + F\cdot + \cdots\cdots \qquad (53)$$

which are exothermic has been uncertain in papers described previously they are well established in other cases[45]. In one, the rate of reaction between nitrogen dioxide and fluorine to form nitryl fluoride was measured between 27 and 70° C[46]. Light absorption by NO_2 was used to follow the reaction. Fluorine was stored in stainless steel bulbs. The rate of the fast reaction was reduced to a convenient value by using a large reaction vessel. The rate was first order in each reactant

and showed no dependence on nitryl fluoride pressure. The mechanism proposed was:

$$NO_2 + F_2 \longrightarrow NO_2F + F\cdot \quad \text{(slow)} \qquad (54)$$

$$NO_2 + F\cdot + M \longrightarrow NO_2F + M \quad \text{(fast)} \qquad (55)$$

Result:

$$k_{54} = 1\cdot6\times10^{12}(\exp - 10\cdot5/RT) \text{ cc mole}^{-1}\text{sec}^{-1}.$$

In another case the reaction between fluorine and chlorine oxide to form $FClO_2$ was studied in the range -46 to -26° C[47]. Nitrogen, oxygen and ClO_2F were added as inerts. The reaction scheme proposed was:

$$F_2 + ClO_2 \longrightarrow FClO_2 + F\cdot \qquad (56)$$

$$F\cdot + ClO_2 \longrightarrow FClO_2 \qquad (57)$$

$$F\cdot + F\cdot + M \longrightarrow F_2 + M \qquad (58)$$

$$F\cdot \text{ wall} \longrightarrow \tfrac{1}{2}F_2 \qquad (59)$$

At low concentration of ClO_2 and low total pressure (56) and (59) were thought only to occur. At high ClO_2 concentration and high total pressure (57) and (58) occurred to a certain degree. The effect of (57) was greater at higher temperatures because of its considerable heat of activation.

Result:

$$k_{56} = 5.5\times10^{10} \exp(-8.5 \pm 0.4/RT) \text{ cc mole}^{-1}\text{sec}^{-1}.$$

CHAPTER 3.

FLUORINATION EXPERIMENTAL.

3·1. AIM OF THE WORK.

The purpose of this work is to determine over a temperature range the rate constants of reactions of the type,

$$X\cdot + RH \longrightarrow HX + R\cdot \qquad (2)$$

where X· is either a fluorine or bromine atom and RH usually an alkane or alkyl halide.

A study of systems containing fluorine or bromine (X_2) and hydrocarbon in large excess can lead to a value for this rate constant. The following reaction scheme is well established.

$X_2 \longrightarrow 2X\cdot$ either photochemically or thermally

$X\cdot + RH \longrightarrow HX + R\cdot$ (2) slow

$R\cdot + X_2 \longrightarrow RX + X\cdot$ (3) fast

chain ending steps.

Reaction (2) is rate-controlling and a measurement of the overall reaction rate will give the rate constant for (2).

Assuming the Arrhenius relationship,

$$k = Ae^{-E/RT}$$

where k is a rate constant, A the Arrhenius A factor and E the experimental activation energy, a plot of log k against the reciprocal of the temperature gives values for A and E.

The values of the experimental A factors can then be compared with those calculated from transition-state theory and perhaps a better understanding of the methods of calculation found.

No such comparison of the activation energies may be made because they cannot be calculated with any accuracy from first principles. In the case of bromine atoms, however, a comparison of activation energies and the strengths of the C-H bonds broken by the attacking bromine atom can lead to values of these bond strengths.

3·2. THE COMPETITIVE METHOD.[37]

The measurement of the absolute rate constants of reaction (2) requires a knowledge of:

(a) The concentration of the hydrocarbon - (RH).

(b) The concentration of the halogen free radical - (X·).

(c) The progress of the reaction - Rate.

The rate constant can then be found from the relationship,

$$\text{Rate} = k_2 (X\cdot)(RH).$$

By carrying out the reaction with a large concentration of hydrocarbon to low conversion the known concentration of RH remains virtually constant throughout the reaction.

(X·) cannot generally be directly determined. In the case of fluorine, owing to its high reactivity, reaction chains are broken on the walls and are difficult to reproduce. It is therefore impossible to rely simply on the known dissociation constant of the diatomic molecule to estimate (F·) as was done in the case of bromine (Chapter 5). However in both cases (X·) could be more easily measured by some concurrent chemical reaction. Since X_2 is used to generate the atoms the dimerization reaction $2X\cdot \longrightarrow X_2$ cannot be used. By introducing two hydrocarbons R_1H and R_2H into the system competition for the atoms can be carried out.

For simultaneous reactions:

$$R_1H + X\cdot \xrightarrow{k_1} HX + R_1 \quad (1) \qquad\qquad R_1 + X_2 \longrightarrow R_1X + X\cdot \quad (3)$$

$$R_2H + X\cdot \xrightarrow{k_2} HX + R_2 \quad (2) \qquad\qquad R_2 + X_2 \longrightarrow R_2X + X\cdot \quad (4)$$

$$\text{Rate (1)} = k_1(X\cdot)(R_1H)$$

$$\text{Rate (2)} = k_2(X\cdot)(R_2H)$$

Hence $$\frac{k_1}{k_2} = \frac{\text{Rate (1)}\ (R_2H)}{\text{Rate (2)}\ (R_1H)}.$$

This ratio can be measured without measuring ($X\cdot$).

If one rate constant is known absolutely, by carrying out a series of reactions in pairs where one rate constant of each pair is related to the known absolute rate constant either directly or indirectly, the absolute rate constants for a whole series of reactions can be found.

The problem is now reduced to measuring Rates (1) and (2). This may be done by two methods (a) and (b):-

(a) The amounts of R_1H and R_2H consumed can be measured:

$$\frac{\text{Rate (1)}}{\text{Rate (2)}} = \frac{-d(R_1H)/dt}{-d(R_2H)/dt} = \frac{k_1(R_1H)}{k_2(R_2H)}$$

$$\frac{-d(R_1H)/(R_1H)}{-d(R_2H)/(R_2H)} = \frac{k_1}{k_2}$$

Integrating $$\frac{k_1}{k_2} = \frac{\ln(R_1H_i) - \ln(R_1H_f)}{\ln(R_2H_i) - \ln(R_2H_f)}$$

where (RH_i) and (RH_f) are the initial and final concentrations of hydrocarbon.

If the amount of reaction is assumed to be small then the approximation $\ln(1 + x) \simeq x$ $(x \rightarrow 0)$ can be made to give

$$\frac{k_1}{k_2} = \frac{\Delta(R_1H)(R_2H)}{\Delta(R_2H)(R_1H)}$$

Thus this method involves the measurement of small changes in large concentrations of hydrocarbon. Although this can be done with a certain amount of accuracy with reactions of similar rate, errors arise where one reaction is much faster than the other and the errors in (R_1H) and (R_2H) are different. This can be partially counterbalanced by appropriate variations in the initial concentrations of hydrocarbon.

A further disadvantage is that the method makes no differentiation of the

types of hydrogen abstracted, although rough estimates can be made[48].

(b) The reaction could be followed by analysis of products characteristic of the initial point of attack of X·. It is seen from the reaction scheme that the alkyl halides are such products. Applying the competitive method we have,

$$\frac{k_1}{k_2} = \frac{(R_1X)(R_2H)}{(R_2X)(R_1H)}$$

where (R_1X) and (R_2X) are the final concentrations of alkyl halides.

Previously small amounts of deuterated products could be measured,[49] but measurement of small amounts of alkyl halides was only made possible with the advent of gas chromatography[50].

Method (b) has been used throughout this work. It is more accurate than method (a) and attack at the three types of hydrogen can be followed. The method would be inaccurate if all radicals R· formed did not attack a halogen molecule. Impurities must be assumed to have the same effect on the two radical types under examination. The dimerization reaction (5) could occur and

$$2R\cdot \longrightarrow R_2 \qquad (5)$$

the product could then undergo hydrogen abstraction. This may have happened in the earlier heavy hydrogen work. However it did not appear to occur in the systems considered here since the radicals formed were reactive enough to react with a halogen molecule before their concentration could build up to give dimerization. Where this reaction did occur, as in the reaction of chlorine atoms with chloroform,[42]

$$2CCl_3\cdot \longrightarrow C_2Cl_6 \qquad (6)$$

extrapolation to zero $\frac{(Cl\cdot)}{(Cl_2)}$ gave a true result.

A more serious error could arise in the systems under consideration if the product formed from halogen attack on the parent hydrocarbon itself under-

went attack faster than the parent hydrocarbon. This effect can be minimised by using large pressures of hydrocarbon and carrying out the minimum of reaction.

Systems cannot be investigated where one reaction is so much faster than the other that, even by adjustment of initial hydrocarbon concentration, enough of the slower formed alkyl halide is not formed for analysis (say 1μ mole) before 10% uptake of the other hydrocarbon occurs. A combination of product attack and this effect creates even larger errors. An increase in reaction vessel size would be the only answer.

3.3. ELEMENTARY FLUORINE.

The history of fluorine compounds spreads over almost two hundred years; but it was not until the latter part of the nineteenth century that investigators attempted the isolation of elementary fluorine. Attempts to prepare fluorine by chemical means all failed (there is still no chemical method) as did the electrolysis of hydrogen fluoride in aqueous solution[51].

In 1886 Moissan[52] prepared fluorine by the electrolysis of anhydrous hydrogen fluoride in potassium fluoride solution (KF.3HF) at boiling methyl chloride temperature using a platinum U-tube cell with platinum electrodes. With the availability of supplies of anhydrous hydrogen fluoride in the 'thirties and the development of suitable anodes two other types of cell were produced using different working temperatures[53]. The temperature was such that at the composition of the electrolyte used the vapour pressure of HF was not greater than 5 cm. The high temperature type (250° C) with electrolyte composition KF.HF[54] was displaced by the medium temperature cell. Most of the present day cells are developments of the latter with electrolyte composition KF.2HF, introduced by Lebeau and Damiens in 1925[55].

Although fluorine can be supplied in cylinders at various pressures[56], both its purity and safety are suspect. A medium temperature cell was therefore used to generate fluorine in situ. It was an I. C. I. General Chemicals Division cell working at 82 ± 5° C with 40-42% HF in molten KF as electrolyte. It had a carbon anode and the base of the cell formed the cathode to help prevent the occurrence of an overvoltage by circulation of the electrolyte over the cathode. The cell could produce up to 7g. of fluorine per hour and carried a maximum current of 10 amps. The reactions at the electrodes are complex. If F^- and HF_2^- are assummed to be in solution the anode reaction could be represented as[57],

$$2F^- = F_2 + 2e \qquad (7)$$

and the cathode

$$2HF_2^- + 2e = H_2 + 4F^- \qquad (8)$$

The quantitative gas analysis after removal of HF(5-15%) claimed by Rudge[58] is F_2 98-99%, O_2 0·5%max. and inerts 1% max. A spray of electrolyte is also emitted.

As fluorine production became easier research into its chemistry has gradually caught up with the rest of the halogens. From 1886 to 1919 six papers were published on elementary fluorine, while from 1919 to 1939 twenty-five papers appeared on fluorine cells and many more on elementary fluorine. The Second World War really put fluorine chemistry on its feet. As more research was done the fear of fluorine became less. In the early days Moissan stressed the dangers involved in the handling of fluorine. Later, however, Leech[53] could quote the statement of G. H. Cady - "In my opinion the hazards of work with fluorine and its compounds have been over-rated ... When treated with the respect which is due to it fluorine is just another substance". This statement is taken as the philosophy of the present work.

Handling of Fluorine:- Dry HF free fluorine will not attack glass. It was found that attack did take place due probably to traces of HF arising from fluorine attack on impurities on the glass or in the tap grease. Storage of fluorine diluted with nitrogen in a five litre bulb was also unsuccessful since no fluorination reaction would take place after a day's storage. Storage in a pyrex tube at -200° C with a liquid oxygen pump-down trap gave peculiar results. Reaction appeared to occur via a less reactive entity. Since it is the custom in industry to "pickle" metal surfaces to form a protective metal fluoride layer,

it was decided that a protective layer would be advantageous for glass as well. Because pyrex has only a small percentage of suitable cations available which would form a non-volatile coating, soft glass was used. It was found that a suitable coating of probably calcium fluoride was formed after about five day's contact with fluorine and fluorine could be stored at -200° C for a week without affecting the results. This method of storage also avoided the need to scrub the fluorine free from HF before collection with sodium fluoride[56] since the vapour pressure of HF at that temperature is zero.

All taps in contact with fluorine were greased with Florube Carbon Grease 'A' supplied by I. C. I. The grease was not however very suitable for high vacuum work since the taps had to be regreased every five days. A good high vacuum grease for fluorine is badly needed.

Collection of Fluorine:- The pickled soft glass bulb (M, Fig. 3·1) of volume 100 ml was attached to the cell by a thin glass (pyrex) tube with a glass-to-metal cone join (B10) at the cell end and a neoprene join to the bulb. The bulb was first flushed out with nitrogen led in from the side arm. The cell was then turned up to maximum fluorine output, the nitrogen flow switched off and the side arm tap closed. After seven amp. hr. generation the two taps on the collector bulb were closed and the cell switched off. The fluorine was then immediately transferred to the storage trap. The first sample was rejected since it always gave anomalous results due probably to traces of oxygen.

3·4. FLUORINATION MATERIALS.

Chromatography:-

(1) Hydrogen (B.O.G. cylinder) was dried by passage over calcium chloride.

(2) Celite (John Mansville) was purified and coated with liquid phase as described by Phillips[59]. It was packed in 4 mm i.d. pyrex columns.

(3) Firebrick (fosalsil No. 6 powder made by Moler Products, Colchester) was washed, dried and sieved before being coated with liquid phase.

Hydrocarbons:-

Hydrocarbon	Source	Analysis
Ethane	B.O.G. cylinder	2% ethylene
ethane	D.S.I.R. ampoule	pure
propane	I.C.I. cylinder	0·6% isobutane, 0·5% propylene
n-butane	B.P. cylinder	pure
isobutane	B.P. "	0·3% propane
neopentane	D.S.I.R. ampoule	pure
cyclopropane	B.O.G. medicinal cylinder	pure
methyl chloride	B.P. cylinder	pure
methane	B.O.G. cylinder	air, 2% ethane + ethylene, 0·5% propane.

With the exception of methane the hydrocarbons were trap distilled from -80 to -183° C and given several degassings. Methane was introduced into the storage bulb through a trap at -183° C which removed most of the hydrocarbon impurities. Several subsequent distillations from -183° C to a liquid oxygen pump-down trap were carried out.

Inert Gases:-

(1) Nitrogen (B.O.G. cylinder) was oxygen free.

(2) Carbon dioxide (I.C.I. drikold) was distilled from -20 to -183° C, rejecting head and tail fractions and given several degassings from -183° C.

Freezing Mixtures:-

Mixture		Temperature ° C
Acetone	- powdered drikold	-80
chloroform	- powdered drikold	-77
ethanol	- powdered drikold	-72
acetone	- lump drikold	-65
ethanol + water (1:1)	- powdered drikold	-35
conc. sulphuric acid + $6H_2O$	- powdered drikold	-40
calcium chloride $6H_2O$ + water (2:1)	- powdered drikold	-30

Boiling Liquids:-

(1) Diethyl ether (35° C) (2) Ethanol (78° C)

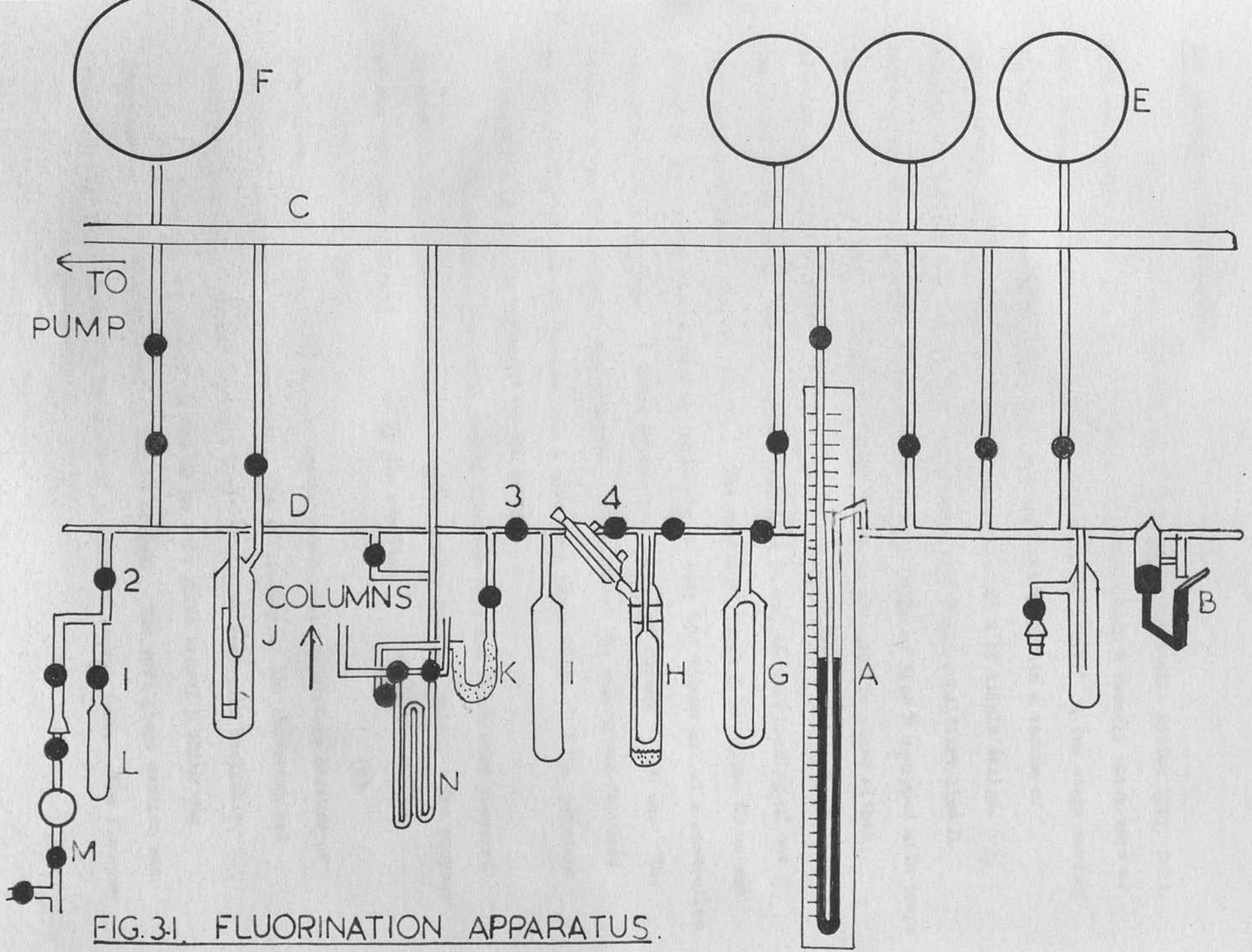


FIG. 3-1. FLUORINATION APPARATUS.

3·5. APPARATUS AND PROCEDURE.

Experiments were carried out in a high vacuum, static system (Fig. 3·1). With the exception of the fluorine storage and collection M vessels which were of soft glass, the apparatus was built entirely of pyrex glass. A two stage mercury diffusion pump backed by a rotary oil pump was used to obtain a vacuum of approximately 10^{-5} mm which was measured on a vacustat B of simple design. Pumping was carried out through the main vacuum line C and subsidiary line D. Hydrocarbons were stored in three 2 litre storage bulbs of type E equipped with traps for degassing purposes. Bulb F of volume 5 litres was used to store either nitrogen or carbon dioxide. The hydrocarbon mixing vessel G was designed with two limbs joined at the top and bottom (volume = 25 cc) so that heating of one limb gave good cyclic thermal mixing. The reaction vessel H of volume 60 cc was joined to the vacuum line with 2 mm capillary to keep the volume not at a controlled temperature to a minimum. I was a preheating vessel of volume ~ 100 cc. The bourdon J was for pressure measurements. Movement of the mirror was followed by observation of the reflection from a lamp on a paper scale. 1 cm. pressure corresponded to 1·1 cm. movement on the scale.

The U-tube K contained sodium fluoride crystals which were prepared by recrystallizing technical sodium fluoride powder from hot water. The purpose of the tube was to absorb fluorine by the reaction

$$NaF + HF \longrightarrow NaHF_2 \qquad (9)$$

However the temperature could not be raised above room temperature because of possibility of product decomposition. The efficiency of the absorbent was therefore doubtful. Porous crystals would also have been more desirable.

Fluorine was stored in the 20 cc soft glass vessel L which was immersed in a pumped-down dewar of liquid oxygen. The soft glass section was joined to the pyrex apparatus by means of a cone and socket join. The fluorine

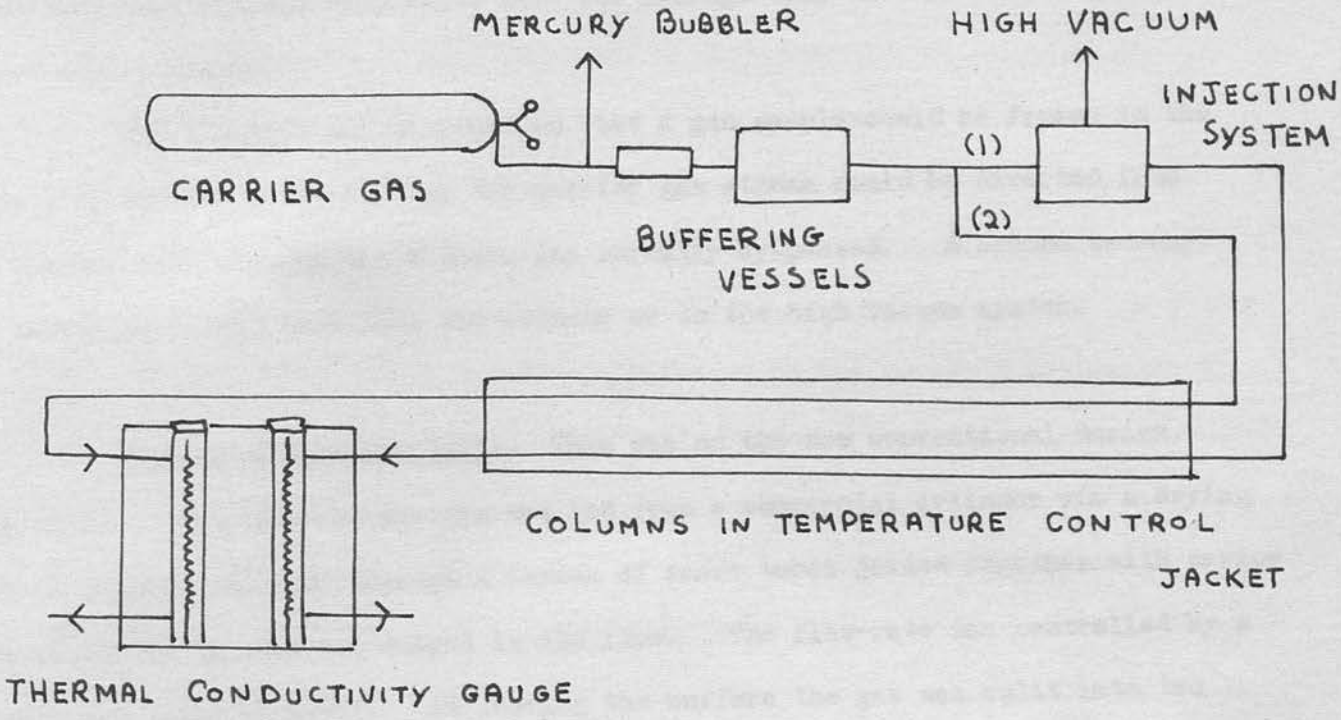


FIG. 3.2. SCHEMATIC DIAGRAM OF CHROMATOGRAPHY SYSTEM.

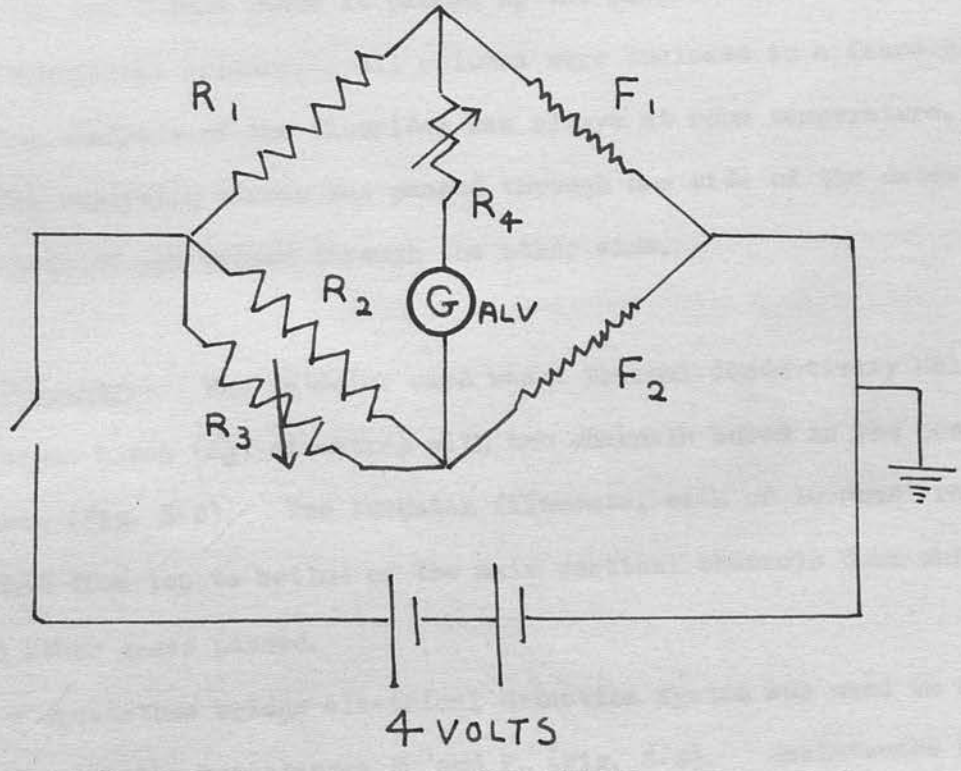


FIG. 3.3. CIRCUIT FOR CONDUCTIVITY DETECTION UNIT.

collection bulb M could be plugged into the storage trap and the collector replaced with a stopper.

The W-tube N was designed so that a gas sample could be frozen in the tube. By turning a two-way tap the carrier gas stream could be diverted from the carrier line through the W which was normally by-passed. A second two-way tap served as a lead back into the columns or to the high vacuum system.

Gas Chromatography Unit:- This was of the now conventional design (Fig. 3·2). Hydrogen carrier gas was led from a commercial cylinder via a drying tube of calcium chloride through a series of short tubes joined together with narrow bore capillary to even out surges in the flow. The flow-rate was controlled by a mercury and water blow-off. On leaving the buffers the gas was split into two streams, one of which passed through a column balanced with the analytical columns so that the flow-rate through both channels was identical. The other stream could be lead through the W-tube where it picked up the sample to be analysed and carried it into the analytical columns. All columns were enclosed in a fibre-glass jacket which, for the analysis of the fluorides, was always at room temperature.

The analysing stream was passed through one side of the detector (Fig. 3·2) while the balancing gas passed through the other side.

Detector:- The detector used was a thermal conductivity cell consisting of a heavy brass block ($3\frac{1}{2}$" diameter) with two channels bored in the position shown in the diagram (Fig. 3·2). Two tungsten filaments, each of 10 ohms' resistance, were stretched from top to bottom of the main vertical channels down which the carrier and other gases passed.

A wheatstone bridge electrical detection system was used in which the two filaments were the resistances F_1 and F_2 (Fig. 3·3). Resistances R_1 and R_2

each of 100 ohms completed the bridge, for which the current was supplied by two 2 volt accumulators. A balance could be obtained with the carrier gas passing by means of the variable resistance R_3 (0-11K ohms).

When the hydrogen gas carried a component over one of the filaments its thermal conductivity effect on the resistance caused an out-of-balance voltage in the bridge. This voltage was fed to a moving-coil galvanometer and the extent of mirror movement followed on a scale. By means of the variable resistance R_4 in series with the galvanometer the sensitivity could be varied according to the amount of product present.

A plot of mirror movement against time (readings were plotted every $\frac{1}{8}$th of a minute) gave peaks which were almost symmetrical.

The Carrier Gas:- Hydrogen was used as carrier gas rather than the more commonly used nitrogen. It gives a more stable base line and greater sensitivity of detection (see below). Interpretation of its chromatograms is also easier. Its higher H.E.T.P. values and explosion hazards are definite disadvantages.

Quantitative Interpretation of Chromatograms:- Quantitative analysis would be simple if the elution area of each component were a direct measure of that component. The signal in the detector is proportional to the difference in thermal conductivity between the carrier gas and component. Average components have thermal conductivities which vary between 0·4 and 0·6 as compared to air. With nitrogen as carrier gas this variation could cause anything up to 30% error unless correction for thermal conductivities are used. Since thermal conductivity $\propto \frac{1}{(\text{Molec. Wt})^{\frac{1}{2}}}$, the conductivities of hydrogen and helium are high (6 and 7 referred to air respectively) and any change in thermal conductivity from component to component

will only be 1-2% in comparison[60].

However it has been found that greater errors do occur and areas neither represent mole % nor wt. % of product[61]. Wt. % would appear to be the nearer to area[62,63].

It is therefore sometimes necessary to multiply each area by a distinctive factor to get the concentration of component present. These calibration factors must be found experimentally since no suitable heat conductivity theory for dilute gas mixtures has been established[64]. The factors must be independent of the range of component concentration to which it is applied. This is generally the case for low concentrations of components[65].

Measurement of Peaks:- It was decided to use a planimeter for the measurement of peak areas, since areas from ($\frac{1}{2}$ peak width X ht.) factors are inaccurate for tall narrow peaks. In such cases greater accuracy could perhaps be obtained by multiplying the peak height by its retention time since, to a first approximation, band widths are proportional to component speed and therefore to retention time. However this method is not entirely satisfactory either, since if viscosities of the components vary, band widths, which are linked to speeds of diffusion, will be entirely different.

A further disadvantage of peak height measurements is their dependence on instrument parameters[63].

Identification of Components:- Because of the difficulties involved in the preparation of the monofluorides they were identified by their elution times from the column. Since they eluted in order of boiling point and were virtually the only higher boiling components present little difficulty was encountered. s-Butyl fluoride prepared by Tedder, Sheffield was run as a check

against which the other elution times could be standardised.

Procedure for a Run:-

Preparation of Hydrocarbon Mixtures:- Before each run the apparatus was pumped down to 10^{-5} mm pressure. Between 5 and 16 cm of one hydrocarbon was measured on the manometer A into the mixing vessel. The mixing vessel tap was then closed, the surplus hydrocarbon was frozen back into its appropriate storage bulb and the measured hydrocarbon transferred from the mixing vessel to the reaction vessel by freezing it down with liquid oxygen. When a similar pressure of the second hydrocarbon had been measured into the mixer and the tubes evacuated, the first hydrocarbon was frozen back into the mixer where the two were thermally mixed by surrounding half the length of the limbs with boiling water for ten minutes. The hydrocarbons were then expanded into the reaction vessel to give a pressure of 4 to 8 cm.

Where a single hydrocarbon was to be used approximately 6 cm was measured directly into the reaction vessel.

Preparation of Fluorine - Inert Gas Mixtures:- When the apparatus had again been pumped down the fluorine was introduced into the reaction vessel by means of a series of expansions, to obviate any danger of a large amount of fluorine being introduced in error.

Tap 1 was opened briefly with taps 2, 3 and 4 closed. Tap 2 was carefully opened until the bourdon registered approximately $\frac{1}{2}$ cm fluorine in the tubes between 2 and 3. With 2 closed, 3 was opened and the fluorine expanded into the preheating vessel where the pressure was made up to 30-40 cm with either nitrogen or carbon dioxide. With tap 3 closed, 4 was briefly opened to intro-

duce the fluorine and inert gas mixture into the reaction vessel containing the hydrocarbon. The fluorine between taps 1 and 2 was pumped away using a water pump, while the surplus inert gas-fluorine mixture was pumped away by the oil pump.

Reaction was extremely rapid and no illumination was required. With the same initial pressures of reactant gas, variation of the reaction time from ½-30 minutes gave the same amounts of products in the same ratios. Consequently normally 3-7 minutes were allowed for reaction and any slow side reactions or decomposition of products which might have occurred were avoided.

The reaction vessel contents were transferred to the chromatography trap for the analysis of the products. Where carbon dioxide was used as inert all the contents could be frozen into the trap with liquid oxygen. When the inert gas was nitrogen, however, the reaction vessel was surrounded with liquid oxygen for five mintues after which the volatile material was pumped through the chromatography trap also surrounded with liquid oxygen. The reaction vessel was heated up and the remaining gases transferred to the chromatography trap with gentle pumping. This procedure prevented the nitrogen from pulling through products with it to the pump.

The products were then analysed and the apparatus pumped out ready for the next run.

CHAPTER 4.

FLUORINATION RESULTS.

4·1. TOPIC NO. 1 - FLUORINATION OF PROPANE.

Most of the preliminary work on developing the method of fluorination was carried out on propane. Experiments were carried out between 36° C and -99° C using nitrogen as an inert gas. Its function was to control the reaction of the fluorine by removing energy in three-body collisions.

Analysis was carried out for n-propyl and isopropyl fluoride. Results are also quoted from analyses of experiments carried out in the presence of other hydrocarbons in later topics using carbon dioxide as the inert gas. Neither the type of hydrocarbon nor the change in the inert gas affected the results.

Chromatography:- Columns of 15' 25% nitrobenzene/firebrick (25-52 mesh) were used at room temperature. Using a hydrogen flow rate of 30 cc/min isopropyl fluoride eluted in ten minutes and n-propyl fluoride in thirteen minutes. Other products were formed depending on the fluorine pressure.

Reactant Pressures:- The average pressures in the reaction vessel were 1 mm fluorine, 4 cm propane and 16 cm nitrogen giving F_2:Propane:N_2 = 1:40:160.

The effect of variation in the fluorine pressure is best seen by considering the complete chromatogram (Table 4·1).

Product 1 arose even when the reactivity of the fluorine had fallen to nil due to bad storage. The peak appeared when a sample of fluorine alone was analysed. It increased with the age of the fluorine and seem to be associated with the fall off in the ratio observed in test runs. It was thought to be a product from the reaction of fluorine on HF with the glass, probably SiF_4.

Table 4·1. Products from Propane Fluorination.

Component	No.	Elution Time min	Rel. Peak Ht. 1mm F_2	4mm F_2
Nitrogen		$2\frac{1}{4}$-$2\frac{1}{2}$		
SiF_4?	1	$2\frac{1}{2}$-$2\frac{3}{4}$	15	60
F_2O?	2	$2\frac{3}{4}$-3	-	3
Propane		3-$4\frac{1}{2}$		
$CH_3CH{=}CH_2$	3	3-$4\frac{1}{2}$	1	4
?	4	$5\frac{1}{2}$	-	6
?	5	8	$\frac{1}{2}$	6
$CH_3CHF.CH_3$	6	10	7	28
$CH_3CH_2CH_2F$	7	13	5	18
$CH_3CF_2CH_3$?	8	14	-	2
$CH_3CH_2CF_2H$?	9	18	-	2

Product 2 was always small and was thought to be an oxide of fluorine. Addition of oxygen ($\frac{1}{2}$ cm) itself to the system slowed down the reaction considerably but did not alter the ratio of the monofluorides appreciably.

Product 3, propylene, could not be accurately analysed for on the tail of propane. Its formation was not fully investigated. It appeared to be in small amount at 1 mm fluorine pressure, rising to a maximum at about 5 mm fluorine. Further increase in fluorine pressure had no effect on its size.

Products 4 and 5 increased with fluorine pressure. They were markedly decreased when the capillary length joining the reaction vessel to the line was decreased. Presumably this allowed quicker mixing on introducing the fluorinating mixture and prevented local concentractions of reaction. Their elution times seem to correspond to fluorine derivatives of propylene.

The nitrogen pressure was varied from 8 cm in Run 2, i.e. $F_2:C_3H_8:N_2$ = 1:60:80 to 23 cm in Run 1 without effect. Variation of the hydrocarbon pressure

from 2 cm in Run 3 to 8 cm in Run 6 had no effect. The effect of changes in the inert gas and hydrocarbon pressures was investigated in all topics. Since no effect was found in most cases, it was decided that nothing was to be gained by tabulating the results for every run. Except in topics 1 and 4 only the results for the extremes of pressures used are quoted in the text.

Mechanism:- The formation of the monofluorides would appear to go by the mechanism,

$$F_2 \longrightarrow 2F^{\bullet} \qquad (1)$$

$$CH_3CH_2CH_3 + F^{\bullet} \xrightarrow{k_{pPr}} CH_3CH_2CH_2^{\bullet} + HF \qquad (2)$$

$$CH_3CH_2CH_2^{\bullet} + F_2 \longrightarrow CH_3CH_2CH_2F + F^{\bullet} \qquad (3)$$

$$CH_3CH_2CH_3 + F^{\bullet} \xrightarrow{k_{sPr}} CH_3CHCH_3^{\bullet} + HF \qquad (4)$$

$$CH_3CHCH_3^{\bullet} + F_2 \longrightarrow CH_3CHFCH_3 + F^{\bullet} \qquad (5)$$

From reactions (2) and (4) which are rate controlling,

$$\frac{k_{pPr}}{k_{sPr}} = \frac{(n\text{-PrF})}{(s\text{-PrF})}$$

Formation of olefin could occur in several ways;

(a) By decomposition of propyl radicals by disproportionation (6)

$$2CH_3CH_2CH_2 \longrightarrow CH_3CH_2CH_3 + CH_3CH = CH_2 \qquad (6)$$

The concentration of radicals was probably too low for this reaction to occur.

(b) Reactions (7) to (9) could occur[4];

$$CH_3CH_2CH_2^{\bullet} + F_2 \longrightarrow HF + F^{\bullet} + CH_3CH = CH_2 \qquad (7)$$

$$CH_3CH = CH_2 + F^{\bullet} \longrightarrow CH_3CHFCH_2^{\bullet} \qquad (8)$$

$$CH_3CHFCH_2^{\bullet} + F_2 \longrightarrow F^{\bullet} + CH_3CHFCH_2F \qquad (9)$$

This mechanism could also explain the formation of products 4 and 5 (Table 4·1).

(c) The fluorides may be "hot" at the moment of their formation and if the excess energy is not removed by a collision with nitrogen HF could split off. If this were the case there should be a relationship between the amount of olefin

formed and the nitrogen pressure. This mechanism would not require the formation of difluorides to any extent and seems the most reasonable.

The difluorides are almost certainly formed from,

$$CH_3CH_2CH_2F + F\cdot \longrightarrow CH_2CH_2CH_2F\cdot + HF \qquad (10)$$

$$CH_2CH_2CH_2F\cdot + F_2 \longrightarrow FCH_2CH_2CHF + F\cdot \qquad (11)$$

$$CH_3CH_2CH_2F + F\cdot \longrightarrow CH_3CH_2CHF\cdot + HF \qquad (12)$$

$$CH_3CH_2CHF\cdot + F_2 \longrightarrow CH_3CH_2CHF_2 + F\cdot \qquad (13)$$

Similarly attack could occur at the secondary position. From the work of Tedder[38] (12) and (13) are less probable.

Example of Calculation for a Run:-

Run No. 4. Temperature of Reaction Vessel = -60° C

Pressures in R.V.

Propane = 4 cm

Nitrogen = 20 cm

Fluorine = 1 mm

Peak area of n-propyl fluoride = 2·10 units.

Peak area of isopropyl fluoride = 0·80 units.

$$\frac{k_{pPr}}{k_{sPr}} = \frac{(n\text{-}PrF)}{(s\text{-}PrF)} = \frac{2\cdot10}{0\cdot80} = 2\cdot62$$

This is the molar ratio of the rate constants and does not take into account the number and type of hydrogens present. As is seen later, with the exception of methyl fluoride all the fluorides had the same sensitivity to the detector so the ratio is a true one.

The results are shown in Table 4·2. Because of the method of introducing the hydrocarbon and inert gas into the reaction vessel the pressures can only be given to the nearest cm.

Table 4·2 Results of Propane Fluorination.

Run No.	Topic No.	Temp° C	Inert Gas (cm) (approx)	C_3H_8 (cm) (approx)	Peak Areas (Units) n-PrF	s-PrF	$\frac{k_{pPr}}{k_{sPr}}$
8	1	36	23 (N_2)	6	1·78	0·70	2·54
9	"	23	16	6	2·06	0·80	2·58
2	"	17	8	6	2·43	0·93	2·61
5	"	"	20	6	1·54	0·60	2·56
4	"	-60	20	4	2·10	0·80	2·62
3	"	-61	8	2	2·18	0·86	2·53
6	"	-99	20	8	1·57	0·63	2·50
7	"	"	12	6	1·84	0·71	2·59
3	4 (a)	25	23 (CO_2)	8	2·13	0·90	2·32
4	"	"	23	4	2·20	0·90	2·44
7	"	"	22	4	2·02	0·84	2·40
8	"	"	22	4	1·88	0·78	2·41
9	"	"	21	4	1·05	0·43	2·44
23	"	"	12	3	0·96	0·39	2·46
24	"	"	11	3	2·12	0·85	2·50
10	"	-30	21	2	1·65	0·68	2·44
11	"	"	20	2	1·79	0·75	2·40
13	"	"	19	4	1·31	0·55	2·54
14	"	"	19	4	1·68	0·70	2·40
28	"	"	23	4	2·80	1·20	2·44
16	"	-60	18	4	3·88	1·50	2·55
17	"	"	18	4	3·01	1·19	2·53
19	"	"	17	4	3·55	1·34	2·64
20	"	"	16	2	1·64	0·68	2·41

Table 4·2 (continued).

Run No.	Topic No.	Temp° C	Inert Gas (cm) (approx)	C_3H_8 (cm) (approx)	Peak Areas (Units) n-PrF	s-PrF	$\frac{k_{pPr}}{k_{sPr}}$
21	4 (a)	-60	15	2	1·34	0·53	2·53
25	"	"	23	3	1·50	0·59	2·54
27	"	"	23	2	2·09	0·82	2·55
29	"	"	20	4	1·87	0·73	2·56
3	3	20	20	3	6·42	2·66	2·41
4	"	"	20	4	6·90	3·36	2·33
6	"	"	20	3	5·34	2·13	2·46
1	4 (b)	"	16 (CO_2)	4	1·70	0·67	2·54
2	"	"	16	2	1·32	0·55	2·40
3	"	"	16	2	2·02	0·86	2·35
4	"	"	15	3	1·83	0·74	2·47
5	"	"	15	2	1·80	0·70	2·57
6	"	-25	12	2	2·43	0·94	2·58
7	"	"	12	2	1·33	0·55	2·42
8	"	"	12	2	2·39	0·92	2·52
10	"	"	12	2	1·32	0·58	2·30
11	"	"	12	2	1·34	0·57	2·35
12	"	-60	20	2	1·43	0·58	2·47
13	"	"	20	2	1·16	0·49	2·37
14	"	"	20	2	2·36	0·92	2·56
15	"	"	18	2	1·43	0·58	2·47
16	"	"	18	2	2·14	0·89	2·41
2	7	20	20 (CO_2)	2	2·49	1·03	2·42
3	"	"	20	2	1·97	0·81	2·49
4	"	-60	19	3	2·03	0·82	2·43

Table 4·2 (continued)

Run No.	Topic No.	Temp° C	Inert Gas (cm) (approx)	C_3H_8 (cm) (approx)	Peak Areas (Units) n-PrF	s-PrF	$\frac{k_{pPr}}{k_{sPr}}$
5	7	-60	19	2	1·85	0·73	2·53
6	"	"	19	3	2·38	0·92	2·57
1	9	20	20 (CO_2)	2	1·97	0·77	2·56
2	"	"	20	2	1·86	0·72	2·58
4	"	"	20	2	2·34	0·96	2·44
5	"	"	14	2	1·77	0·70	2·53
12	"	"	16	2	1·29	0·52	2·48
13	"	"	16	2	1·60	0·65	2·46
14	"	"	16	2	1·15	0·48	2·40
15	"	"	16	2	1·28	0·49	2·40
16	"	"	16	2	0·92	0·38	2·60
17	"	"	16	2	0·93	0·38	2·42
22	"	"	10	2	1·77	0·75	2·45
23	"	"	10	2	1·63	0·66	2·36
18	9	-60	15	2	1·18	0·49	2·41
19	"	"	15	2	1·65	0·68	2·43
20	"	"	14	2	1·59	0·61	2·60
21	"	"	14	2	2·22	0·88	2·52
24	"	"	12	2	1·34	0·52	2·57
25	"	"	12	2	1·80	0·69	2·60

Total Runs = 74 Arithmetic Mean = 2·48

Standard Deviation = 0·08

Result:- $\frac{k_{pPr}}{k_{sPr}} = 2·48 \pm 0·08$

4·2. Topic No. 2 - Fluorination of n-Butane.

Runs were carried out on n-butane between +20° C and -60° C using nitrogen as the inert gas and analysing for n-butyl and s-butyl fluoride. Results are also quoted for runs carried out in the presence of other hydrocarbons using carbon dioxide as the inert gas. The results with CO_2 gave slightly lower values for $k_{pn\text{-}Bu}/k_{sn\text{-}Bu}$, due probably to the lower boiling secondary fluoride being pumped through with the nitrogen. For this reason CO_2 was preferred for later work.

Chromatography:- Columns of 10' 25% dinonyl phthalate / firebrick (25-52 mesh) plus 2' 25% nitrobenzene / washed celite were used at room temperature. With a carrier gas flow rate of 30cc/min s-Bu F eluted in 27 min. and n-Bu F in 34 min. Only traces of difluorides were detected. A small peak of butylene eluted in 12 min.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm fluorine, 4 cm propane and 16 cm nitrogen giving $F_2:n\text{-}C_4H_{10}:N_2 = 1:40:160$.

Changed in nitrogen and fluorine pressures had no effect on the results within the pressure limits used (Table 4·3).

The hydrocarbon pressure was varied from 2 cm in Run 6 to 8 cm in Run 7 without effect.

The effect of changes in the fluorinating mixture on olefin formation was cursorily investigated. There is some evidence that olefin depends on nitrogen pressure. The concentration of olefin also appears to reach a maximum which could perhaps be explained by secondary fluorination of the olefin itself.

Where $k_{pn\text{-}Bu}$ and $k_{sn\text{-}Bu}$ are the rate constants of

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\cdot + HF$$

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CHCH_3\cdot + HF$$

respectively, then

$$\frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}} = \frac{(n\text{-}BuF)}{(s\text{-}BuF)}$$

The results are tabulated in Table 4·3.

Table 4·3 Results of n-Butane Fluorination.

Run No.	Topic No.	Temp° C	$k_{pn\text{-}Bu}/k_{sn\text{-}Bu}$	$n\text{-}C_4H_8$ Rel. Peak Ht.	F_2:n-C_4H_{10}:N_2
1	2a (inert:nitrogen)	20	1·37	10	1: 40 :160
2	"	"	1·42	6	1: 40 :180
4	"	"	1·42	14	1: 40 :120
9	"	"	1·35	9	2: 40 :160
10	"	"	1·38	7	1·5: 40 :160
18	"	"	1·30		
14	"	-30	1·33		
15	"	"	1·38		
8	"	-58	1·36		
5	"	"	1·33		
6	"	-65	1·43		
7	"	"	1·32		
3	"	"	1·32		
11	"	-80	1·40		
1	2b (inert:CO_2)	20	1·31		
2	"	"	1·26		
5	"	"	1·20		
10	"	"	1·26		
11	"	"	1·02		
12	"	"	1·23		
13	"	"	1·28		
15	"	"	1·29		
16	"	"	1·16		
17	"	"	1·17		

Table 4·3 (continued)

Run No.	Topic No.	Temp° C	$\frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}}$	Run No.	Topic No.	Temp° C	$\frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}}$
18	2b (inert:CO_2)	20	1·10	15	4a (inert:CO_2)	-30	1·27
19	"	"	1·07	28	"	"	1·46
21	"	"	1·21	16	"	-60	1·37
23	"	"	1·27	17	"	"	1·35
24	"	"	1·19	19	"	60	1·43
25	"	"	1·25	20	"	"	1·37
26	"	"	1·26	21	"	"	1·40
27	"	"	1·24	25	"	"	1·35
28	"	"	1·27	26	"	"	1·42
8	"	-35	1·20	22	"	"	1·40
22	"	"	1·26	27	"	"	1·31
3	"	-65	1·26	29	"	"	1·46
4	"	"	1·25	30	"	"	1·46
4	4a (inert:CO_2)	20	1·28	1	5 (inert:CO_2)	20	1·33
7	"	"	1·22	2	"	"	1·20
8	"	"	1·22	3	"	"	1·36
9	"	"	1·21	4	"	"	1·27
23	"	"	1·33	5	"	"	1·31
24	"	"	1·40	6	"	"	1·23
10	"	-30	1·46	23	"	"	1·44
11	"	"	1·28	9	"	-25	1·45
12	"	"	1·30	10	"	"	1·42
13	"	"	1·34	11	"	"	1·38
14	"	"	1·35	20	"	"	1·31

Table 4·3 (continued)

Run No.	Topic No.	Temp° C	$k_{pn\text{-}Bu}/k_{sn\text{-}Bu}$	Run No.	Topic No.	Temp° C	$k_{pn\text{-}Bu}/k_{sn\text{-}Bu}$
21	5 (inert:CO_2)	20	1·41	13	4b (inert:CO_2)	-60	1·17
22	"	"	1·44	14	"	"	1·21
7	"	"	1·46	15	"	"	1·24
8	"	"	1·45	16	"	"	1·20
12	"	-60	1·45	1	8 (inert:CO_2)	20	1·20
13	"	"	1·21	2	"	"	1·24
14	"	"	1·37	3	"	"	1·22
15	"	"	1·42	4	"	"	1·23
19	"	"	1·45	5	"	"	1·24
16	"	"	1·44	6	"	"	1·32
17	"	"	1·45	11	"	"	1·30
18	"	"	1·31	21	"	"	1·20
2	4b (inert:CO_2)	20	1·29	22	"	"	1·29
3	"	"	1·30	13	"	-25	1·28
5	"	"	1·38	14	"	"	1·30
11	"	"	1·25	15	"	"	1·26
1	"	"	1·29	16	"	"	1·30
4	"	"	1·29	17	"	"	1·24
6	"	-25	1·38	18	"	"	1·25
7	"	"	1·23	7	"	-60	1·36
9	"	"	1·26	8	"	"	1·36
10	"	"	1·20	12	"	"	1·28
12	"	-60	1·16	19	"	"	1·23

Table 4·3 (continued)

Run No.	Topic No.	Temp° C	$\frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}}$
20	8 (inert:CO_2)	-60	1·31

Total runs = 124

Arithmetic mean = 1·30

Standard deviation = 0·09

Results:

$$\frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}} = 1{\cdot}30 \pm 0{\cdot}09.$$

4·2. Topic No. 3 - Fluorination of Isobutane.

Runs quoted were carried out on isobutane alone between 20° C and -60° C using CO_2 as the inert gas. Analysis was made for tert. butyl and isobutyl fluoride. Results are also quoted for runs carried out in the presence of other hydrocarbons which were all in agreement.

Chromatography:- Columns of 12' 25% diethyl phthlate / washed celite plus 5' 25% diethyl phthalate / firebrick (25-52 mesh) plus 2' 25% nitrobenzene / washed celite were used. With a flow rate of 40 cc/min t-BuF eluted in 18 min and i-BuF in 26 min. A small peak of isobutane eluted in $12\frac{1}{2}$ min.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm fluorine, 4 cm isobutane and 18 cm CO_2, giving F_2:i-C_4H_{10}:CO_2 = 1:40:180.

Changes in the CO_2 pressure had no effect on the ratio of the monofluorides (Table 4·4). The ratio of total fluorides to olefin was also followed with changes in CO_2 pressure. The results indicate that the amount of olefin formed was never much in excess of 5-8% of the total products. However it is unlikely that it was derived completely from one of the monofluorides alone and not the other. It is unlikely that its effect on $k_{ti\text{-}Bu}/k_{pi\text{-}Bu}$, if any, will exceed a 3% error.

There does not appear to be a relationship between the CO_2 pressure and olefin formation. This is probably due to inconsistencies in the results arising from variation in the fluorine / hydrocarbon ratio which was difficult to measure.

Variation in the isobutane pressure from 2 cm (Run 3) to 8 cm (Run 8) had no effect.

Where $k_{pi\text{-}Bu}$ and $k_{ti\text{-}Bu}$ are the rate constants of

$$F\cdot + (CH_3)_3CH \longrightarrow (CH_3)_2C.CH_2\cdot + HF$$

and $$F\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3C\cdot + HF$$

respectively, then

$$\frac{k_{pi\text{-}Bu}}{k_{ti\text{-}Bu}} = \frac{(i\text{-BuF})}{(t\text{-BuF})}$$

The results are tabulated in Table 4·4.

Table 4·4 Results of Isobutane Fluorination.

Run No.	Temp° C	CO_2 (cm)	$\frac{k_{pi\text{-}Bu}}{k_{ti\text{-}Bu}}$	Total Fluorides / $i\text{-}C_4H_8$
2	20	27	6·26	22·0
3	"	25	6·10	20·0
5	"	25	6·36	17·2
6	"	25	6·40	19·3
7	"	30	6·58	14·1
8	"	15	6·32	16·5
9	"	5	5·52	16·1
19	"	30	6·78	20·2
10	-60	20	5·98	-
11	"	20	6·75	-
12	"	18	6·46	-
13	"	18	6·53	-
14	"	16	6·56	-
16	"	16	6·75	-
17	"	12	6·68	-
18	"	12	6·76	-

Total runs = 16 Arithmetic mean = 6·41

Standard deviation = 0·34

Result:

$$\frac{k_{pi\text{-}Bu}}{k_{ti\text{-}Bu}} = 6{\cdot}41 \pm 0{\cdot}34$$

4·4 Topic No. 4 (b) Fluorination of n-Butane versus Propane.

Runs were carried out between 20° C and -60° C on mixtures of n-butane and propane using CO_2 as the inert gas. Analysis was made for n-propyl, isopropyl, n-butyl and s-butyl fluoride.

Chromatography:- Columns of 12' 25% diethyl phthalate / washed celite plus 2' 25% nitrobenzene / washed celite plus 5' diethyl phthalate / firebrick (25-52 mesh) were used at room temperature. A flow rate of 30cc/min eluted s-PrF in 12½ min, n-PrF in 15½ min, s-BuF in 30 min and n-BuF in 39 min. Separation of s-PrF and a small peak of n-butene was poor.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm F_2, 4·4 cm hydrocarbon and 16 cm CO_2 giving F_2:hyd.:CO_2 = 1:44:160.

The pressures of hydrocarbon were varied between n-butane 2·00 cm, propane 2·50 cm (Run 15) and n-butane 2·53 cm, propane 1·93 cm (Run 16). The average pressures used were n-butane 2·15 cm and propane 2·20 cm. (The ratios in Table 4·5 should be divided by three to obtain relative pressures in the reaction vessel).

Where k_{pPr}, k_{sPr}, $k_{pn\text{-}Bu}$ and $k_{sn\text{-}Bu}$ are the rate constants of

$$F\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2\cdot + HF$$

$$F\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CHCH_3\cdot + HF$$

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\cdot + HF$$

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CHCH_3\cdot + HF$$

respectively, then

$$\frac{k_{pPr}}{k_{pn\text{-}Bu}} = \frac{(n\text{-PrF})}{(n\text{-BuF})} \times \frac{(n\text{-Bu})}{(Pr\ )}$$

and $\frac{k_{sPr}}{k_{sn\text{-}Bu}} = \frac{(s\text{-}PrF)}{(s\text{-}BuF)} \times \frac{(n\text{-}Bu)}{(Pr\ )}$

Example of a Calculation.

Run 11 Temp. of Reaction Vessel = -60° C

Pressures of Reactants in R. V.

Propane	2·24 cm
n-Butane	2·36 cm
CO_2	18 cm
Fluorine	1 mm

Peak Area of n-PrF = 1·34 units. Peak Area of s-PrF = 0·57 units.

Peak Area of n-BuF = 1·24 units. Peak Area of s-BuF = 0·99 units.

$$\frac{k_{pPr}}{k_{sPr}} = \frac{(n\text{-}PrF)}{(s\text{-}PrF)} = \frac{1·34}{0·57} = 2·35 \qquad \frac{k_{pn\text{-}Bu}}{k_{sn\text{-}Bu}} = \frac{(n\text{-}BuF)}{(s\text{-}BuF} = \frac{1·24}{0·99} = 1·25$$

$$\frac{k_{pPr}}{k_{sn\text{-}Bu}} = \frac{(s\text{-}PrF)}{(n\text{-}BuF)} \times \frac{(n\text{-}Bu)}{(Pr\ )} = \frac{1·34}{1·24} \times \frac{2·36}{2·24} = 1·14$$

$$\frac{k_{sPr}}{k_{sn\text{-}Bu}} = \frac{(s\text{-}PrF)}{(s\text{-}BuF)} \times \frac{(n\text{-}Bu)}{(Pr\ )} = \frac{0·57}{0·99} \times \frac{2·36}{2·24} = 0·60$$

The results are shown in Table 4·5.

The results in Topic 4a where CO_2 was absorbed before analysis on sofnolite were scattered for the propane / n-butane ratios.

Table 4·5 Results of n-Butane / Propane Fluorination.

Run No.	Temp° C	n-Butane (cm) / Propane (cm)	Peak Areas (Units) s-PrF	n-PrF	s-BuF	n-BuF	$\frac{k_{pPr}}{k_{pn\text{-}Bu}}$	$\frac{k_{sPr}}{k_{sn\text{-}Bu}}$
2	20	5·80/6·00	0·55	1·32	0·87	1·12	1·14	0·61
3	"	6·00/6·00	0·86	2·02	1·56	2·03	1·16	0·62
5	"	6·95/7·10	0·74	1·83	1·20	1·55	1·16	0·61
11	"	7·08/6·72	0·57	1·34	0·99	1·24	1·14	0·60
6	-25	7·27/7·08	0·94	2·43	1·70	2·35	1·06	0·56
7	"	6·90/7·32	0·55	1·33	1·02	1·25	1·00	0·52
8	"	6·30/6·30	0·92	2·39	-	2·04	1·14	-
9	"	7·02/6·84	-	1·69	1·42	1·79	0·96	-
10	"	7·33/6·79	0·58	1·32	1·10	1·31	1·09	0·51
12	-60	6·40/6·40	0·58	1·43	1·08	1·25	1·14	0·54
13	"	6·25/6·40	0·49	1·16	0·83	0·96	1·18	0·57
14	"	6·62/6·18	0·92	2·36	1·85	2·24	1·14	0·54
15	"	6·00/7·51	0·58	1·43	0·86	1·03	1·11	0·54
16	"	7·60/5·80	0·89	2·14	1·17	1·50	1·14	0·61
		Total runs				=	14	12
		Arithmetic Mean				=	1·11	0·56
		Standard deviation				=	0·06	0·04

Results:

$$\frac{k_{pPr}}{k_{pn\text{-}Bu}} = 1{\cdot}11 \pm 0{\cdot}06 \qquad \frac{k_{sPr}}{k_{sn\text{-}Bu}} = 0{\cdot}56 \pm 0{\cdot}04$$

4·5. Topic No. 5 Fluorination of n-Butane versus Isobutane.

Runs were carried out between 20° C and -60° C on mixtures of n-butane and isobutane using CO_2 as the inert gas. Analysis was made for n-butyl, s-butyl, isobutyl and t-butyl fluoride.

Chromatography:- The columns and elution times were as for Topics 3 and 4. i-BuF and s-BuF were not separated absolutely. Lengthening of the columns would have been detrimental to the already tailing n-BuF peak.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm F_2, 5 cm hydrocarbon and 16 cm CO_2 giving F_2:hyd.:CO_2 = 1:50:160.

The pressures of hydrocarbon were varied between isobutane 2·16 cm, n-butane 1·62 cm (Run 19) and isobutane 3·34 cm, n-butane 4·34 cm (Run 23). The average pressures used were isobutane 2·51 cm and n-butane 2·50 cm.

Care had to be taken not to exceed the vapour pressure of n-butane at -60° C and cause an error in the measured hydrocarbon ratio.

Where $k_{pn\text{-}Bu}$ and $k_{pi\text{-}Bu}$ are the rate constants of

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\cdot + HF$$

and $$F\cdot + (CH_3)_3CH \longrightarrow (CH_3)_2CH.CH_2\cdot + HF$$

respectively, then

$$\frac{k_{pi\text{-}Bu}}{k_{pn\text{-}Bu}} = \frac{(i\text{-}BuF)}{(n\text{-}BuF)} \times \frac{(n\text{-}Bu)}{(i\text{-}Bu)}$$

The results are shown in Table 4·6.

Table 4·6. Results of Isobutane / n-Butane Fluorination.

Run No.	Temp° C	$\frac{k_{pi\text{-}Bu}}{k_{pn\text{-}Bu}}$	Run No.	Temp° C	$\frac{k_{pi\text{-}Bu}}{k_{pn\text{-}Bu}}$
1	20	1·55	20	-25	1·53
3	"	1·59	21	"	1·51
4	"	1·61	22	"	1·49
5	"	1·57	12	-60	1·56
6	"	1·53	13	"	1·65
23	"	1·55	14	"	1·66
9	-25	1·60	15	"	1·66
10	"	1·52	19	"	1·55
11	"	1·49			

Total runs = 17 Arithmetic mean = 1·57

Standard deviation = 0·06

Result:

$$\frac{k_{pi\text{-}Bu}}{k_{pn\text{-}Bu}} = 1{\cdot}57 \pm 0{\cdot}06$$

4·6. Topic No. 6 Fluorination of Isobutane versus Neopentane.

Runs were carried out between 20° C and -60° C on mixtures of isobutane and neopentane using CO_2 as the inert gas. Analysis was made for isobutyl and neopentyl fluoride.

Chromatography:- Columns of 12' 25% diethyl phthalate / washed celite plus 2' 25% nitrobenzene / washed celite were used at room temperature. A flow rate of 40cc/min eluted t-BuF in 9½ min, i-BuF in 13 min and neoPF in 18 min. Since a small unidentified peak eluted with t-BuF the latter is not quoted.

Pressures of Reactants:- The average pressures used were 1 mm F_2, 3·5 cm hydrocarbon and 16 cm CO_2 giving F_2:hyd.:CO_2 = 1:35:160.

The pressures of hydrocarbon were varied between isobutane 1·95 cm, neopentane 1·28 cm (Run 1) and isobutane 1·50 cm, neopentane 1·72 cm (Run 10). The average pressures used were isobutane 1·90 and neopentane 1·60 cm.

Where k_{neoP} and $k_{pi\text{-}Bu}$ are the rate constants of

$$F\cdot + (CH_3)_4C \longrightarrow (CH_3)_3C.CH_2\cdot + HF$$

and $$F\cdot + (CH_3)_3CH \longrightarrow (CH_3)_2CH.CH_2\cdot + HF$$

respectively, then

$$\frac{k_{neoP}}{k_{pi\text{-}Bu}} = \frac{(neoPF)}{(i\text{-}BuF)} \times \frac{(i\text{-}Bu)}{(neoP)}$$

The results are shown in Table 4·7.

Table 4·7. Results of Neopentane / Isobutane Fluorination.

Run No.	Temp° C	$\frac{k_{neoP}}{k_{pi\text{-}Bu}}$	Run No.	Temp° C	$\frac{k_{neoP}}{k_{pi\text{-}Bu}}$
1	20	1·14	13	-25	1·24
2	"	1·24	14	"	1·30
3	"	1·20	6	-60	1·20
4	"	1·23	7	"	1·23
5	"	1·17	8	"	1·25
11	-25	1·22	9	"	1·15
12	"	1·25	10	"	1·23

Total runs = 14 Arithmetic mean = 1·22

Standard deviation = 0·04

Result:

$$\frac{k_{neoP}}{k_{pi\text{-}Bu}} = 1{\cdot}22 \pm 0{\cdot}04$$

4·7. Topic No. 7 Fluorination of Cyclopropane versus Propane.

Runs were carried out on mixtures of cyclopropane and propane between 20° C and -60° C, analysing for n-propyl, isopropyl and cyclopropyl fluoride. CO_2 was used as the inert gas.

Chromatography:- The same columns and conditions were used as in Topic 4. The elution times were s-PrF 12½ min, n-PrF 15½ min and c-PrF 18 min. Other products were formed. However only a peak eluting in 17 min was of importance. Peaks eluting in 24½, 28½, 32 and 40 min were very small and probably arose from secondary fluorination.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm fluorine, 4·6 cm hydrocarbon and 26 cm CO_2 giving F_2:hyd.:CO_2 = 1:46:260. The CO_2 pressure was found to be critical. Below ~ 20 cm CO_2 pressure the cyclopropyl fluoride decomposed or rearranged to give a product eluting in 17 min. At lower CO_2 pressures this was a major product as is shown by the following approximate observations.

CO_2 pressure cm	Cyclopropyl fluoride / Rearranged product
30	∞
22	∞
10	1·12
15	2·60

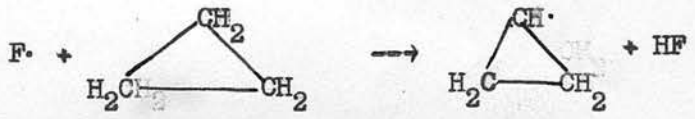
From the similarity in their elution times it might be deduced that the new product had the same number of carbons as cyclopropyl fluoride and was probably a rearrangement of the hot molecule created by the attack of a fluorine atom on the cyclopropane. Sufficient CO_2 pressure prevented this by removal of the excess

energy. From the work of McNesby and Gordon[66] who showed the formation of allylic radicals from cyclopropyl radicals at 375° C, it is probable that this product was allylic fluoride $CH_2FCH = CH_2$. This would have a similar elution time. However $CH_3CH = CHF$ or $CH_3CF = CH_2$ cannot be ruled out. By working with CO_2 pressures in excess of 20 cm the formation of the rearranged product was avoided and the cyclopropyl fluoride measured with accuracy.

The pressures of hydrocarbon were varied between propane 2·74 cm, cyclopropane 2·25 cm (Run 1) and propane 2·12 cm, cyclopropane 2·95 cm (Run 12). The average pressures used were propane 2·41 cm and cyclopropane 2·22 cm.

Although the room temperature runs gave consistent results, the runs at -60° C were slightly irreproducible. This was thought at first to be due to attack of HF on cyclopropane which would give mainly $CH_3CH_2CH_2F$ and some CH_3CHFCH_3[67]. The results were not affected when the reactants were left in the reaction vessel for 30 min after all fluorination had ceased. However the ratio n-PrF/c-PrF appeared to increase with the age of fluorine used and the time it stood in the preheating vessel. This would indicate that the competitive fluorination was affected by excess impurity, probably HF. It was decided that more reliable results would be obtained from the n-butane / cyclopropane system where the latter could not give rise to fluorides of the former.

Where k_{cPr}, k_{pPr} and k_{sPr} are the rate constants of



$F\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2\cdot + HF$

and $F\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CHCH_3\cdot + HF$

respectively, then

$$\frac{k_{pPr}}{k_{cPr}} = \frac{(n\text{-}PrF)}{(c\text{-}PrF)} \times \frac{(c\text{-}Pr)}{(Pr)}$$

and $$\frac{k_{sPr}}{k_{cPr}} = \frac{(s\text{-}PrF)}{(c\text{-}PrF)} \times \frac{(c\text{-}Pr)}{(Pr)}$$

The results are given in Table 4·8.

Table 4·8 Results of Propane / Cyclopropane.

Run No.	Temp° C	$\frac{k_{pPr}}{k_{cPr}}$	$\frac{k_{sPr}}{k_{cPr}}$	Run No.	Temp° C	$\frac{k_{pPr}}{k_{cPr}}$	$\frac{k_{sPr}}{k_{cPr}}$
1	20	0·91	0·37	10	-25	1·06	0·46
2	"	0·98	0·38	11	-60	1·03	0·42
3	"	0·97	0·41	12	"	1·19	0·49
4	"	0·97	0·43	13	"	1·07	0·45
5	"	1·12	0·45	14	"	1·15	0·48
20	"	1·19	0·53	15	"	1·13	0·49
21	"	1·00	-	16	"	1·33	0·52
22	"	1·04	0·44	17	"	1·46	0·50
6	-25	0·99	0·41	18	"	1·15	0·49
7	"	0·97	-	19	"	1·13	0·53
8	"	0·93	0·40	23	"	0·99	-
9	"	0·95	0·44	24	"	1·29	-
				25	"	1·36	-
				Total runs	=	25	20
				Arithmetic mean	=	1·13	0·45
				Standard deviation	=	0·15	0·05

Results:

$$\frac{k_{pPr}}{k_{c-Pr}} = 1{\cdot}13 \pm 0{\cdot}15 \qquad \frac{k_{sPr}}{k_{c-Pr}} = 0{\cdot}45 \pm 0{\cdot}05$$

4·8. Topic No. 8 Fluorination of Cyclopropane versus n-Butane.

Runs were carried out on mixtures of cyclopropane and n-butane between 20° C and -60° C using CO_2 as the inert gas. Analysis was made for n-butyl, s-butyl and cyclopropyl fluoride.

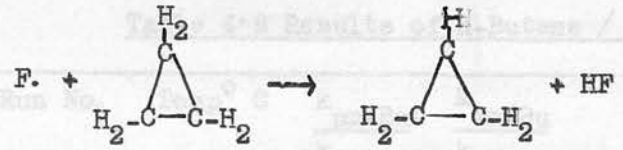
Chromatography:- Columns of 12' 25% diethyl phthalate / washed celite plus 5' 25% diethyl phthalate / firebrick (25-52 mesh) were used. With a flow rate of 30cc/min the elution times were c-PrF 14 min, s-BuF 21 min and n-BuF 29 min. A small peak of n-butene appeared in 12 min and small peaks of secondary fluorination derivatives in 17, 19 and 25 min. The product thought to be allyl fluoride in Topic 7 eluted in 13 min.

Reactant Pressures:- The average pressures used in the reaction vessel were 1 mm fluorine, 5 cm hydrocarbon and 26 cm CO_2 giving F_2:hyd.:CO_2 = 1:50:260. The cyclopropyl fluoride formation showed the same pressure dependence as in Topic 7.

The pressures of hydrocarbon were varied between n-butane 3·82 cm, cyclopropane 3·26 cm (Run 2) and n-butane 2·86 cm, cyclopropane 2·80 cm (Run 5) without effect. The average pressures used were n-butane 2·66 cm and cyclopropane 2·34 cm.

The ratio n-BuF/c-PrF was less dependent on the age of the fluorine than was n-PrF/c-PrF in Topic 7. There was little sign of an activation energy difference.

Where k_{cPr}, $k_{pn\text{-}Bu}$ and $k_{sn\text{-}Bu}$ are the rate constants of



$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\cdot + HF$$

$$F\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CHCH_2CH_3\cdot + HF$$

respectively, then

$$\frac{k_{pn\text{-}Bu}}{k_{c\text{-}Pr}} = \frac{(n\text{-}BuF)}{(c\text{-}PrF)} \times \frac{(c\text{-}Pr)}{(n\text{-}Bu)}$$

$$\frac{k_{sn\text{-}Bu}}{k_{c\text{-}Pr}} = \frac{(s\text{-}BuF)}{(c\text{-}PrF)} \times \frac{(c\text{-}Pr)}{(n\text{-}Bu)}$$

The results are given in Table 4·9.

Table 4·9 Results of n-Butane / Cyclopropane Fluorination.

Run No.	Temp° C	$\frac{k_{pn\text{-}Bu}}{k_{cPr}}$	$\frac{k_{sn\text{-}Bu}}{k_{cPr}}$	Run No.	Temp° C	$\frac{k_{pn\text{-}Bu}}{k_{cPr}}$	$\frac{k_{sn\text{-}Bu}}{k_{cPr}}$
1	20	1·01	0·84	17	-25	1·06	0·86
2	"	1·10	0·89	18	"	1·01	0·81
3	"	1·01	0·83	9	-50	0·99	0·78
5	"	1·07	0·87	10	"	0·99	0·77
6	"	1·04	0·78	7	-60	0·96	0·71
11	"	1·07	0·77	8	"	1·02	0·76
13	-25	0·93	0·74	12	"	0·95	0·75
14	"	1·03	0·79	19	"	1·17	0·96
15	"	1·01	0·81	20	"	1·00	0·76
16	"	0·92	0·71				
				Total runs	=	19	19
				Arithmetic mean	=	1·02	0·80
				Standard deviation	=	0·06	0·06

Results:

$$\frac{k_{pn\text{-}Bu}}{k_{cPr}} = 1{\cdot}02 \pm 0{\cdot}06 \qquad \frac{k_{sn\text{-}Bu}}{k_{cPr}} = 0{\cdot}80 \pm 0{\cdot}06$$

4·9. Topic No. 9 Fluorination of Ethane versus Propane.

Runs were carried out on mixtures of ethane and propane between 20° C and -60° C using CO_2 as the inert gas. Analysis was made for n-propyl, isopropyl and ethyl fluoride.

Chromatography:- Columns of 15' 25% diethyl phthalate / washed celite plus 10' 25% diethyl phthalate / firebrick (25-52 mesh) were used. With a flow rate of 30cc/min the elution times were EtF 6 min, s-PrF 11½ min and n-PrF 20 min. Small peaks of propylene and ethylene appeared in 2¼ and 4 min respectively.

Reactant Pressures:- The average pressures used were 1·5 mm fluorine, 4·3 cm hydrocarbon and 25 cm CO_2, giving F_2:hyd.:CO_2 = 1·5:43:250. The effect of variation in the CO_2 pressure is shown in Table 4·10. It is difficult to decide whether the difference in the results at 25° C and -60° C is due to an activation energy or dependence on the inert gas pressure. At 20° C, although the ratio k_{pPr}/k_{sPr} was consistent throughout, when the CO_2 pressure fell below 19 cm the ratio k_{Et}/k_{pPr} fell from 1·07 to 0·99 in runs 12, 13, 14 and 15. Because of this only results with high CO_2 pressures were accepted.

Results at -60° C were similar to runs 12-15 even at high CO_2 pressures. At a CO_2 pressure of 14 cm the result fell slightly (Run 25).

The lower results at -60° C with high CO_2 pressure could be explained if for some reason the inert gas was not functioning as efficiently as an energy remover at low temperatures. Although at lower temperatures the velocity and therefore the momentum of molecules on collision will be less and the number of collisions also will be less, the effect on the efficiency of energy removal should be small. Any temperature effect on the rate of decomposition of products (perhaps into HF and olefin) should also be negligible.

While there seems to be some argument for an inert gas pressure dependence, it is doubtful if the factors mentioned could cause a 10% fall in the results. It has therefore been assumed that the effect was due to an activation energy difference. This is a little surprising in view of the absence of energy differences in previous topics.

The pressures of each hydrocarbon were varied from propane 1·97 cm, ethane 2·33 cm (Run 1) to propane 2·41 cm and ethane 1·93 cm (Run 5) without effect. The average pressures used were ethane 2·00 cm and propane 2·31 cm.

Where k_{Et} and k_{pPr} are the rate constants of

$$F\cdot + CH_3CH_3 \longrightarrow HF + CH_3CH_2\cdot$$

and $$F\cdot + CH_3CH_2CH_3 \longrightarrow HF + CH_3CH_2CH_2\cdot$$

respectively, then

$$\frac{k_{Et}}{k_{pPr}} = \frac{(EtF)}{(n\text{-}PrF)} \times \frac{(Pr)}{(Et)}$$

The results are shown in Table 4·10 and the Arrhenius plot in Fig. 4·1.

Table 4·10 Results of Ethane / Propane Fluorination.

Run No.	CO_2 Press. (cm)	Temp T (°K)	$\frac{k_{Et}}{k_{pPr}}$	Run No.	CO_2 Press. (cm)	Temp T (°K)	$\frac{k_{Et}}{k_{pPr}}$
1	25	293	1·13	10	20	213	0·91
2	"	"	1·13	18	30	"	0·99
3	"	"	1·15	19	30	"	0·99
4	24	"	1·09	20	29	"	1·02
5	24	"	1·15	21	28	"	0·96
16	25	"	1·09	24	20	"	0·93
17	30	"	1·17	25	14	"	0·89
22	27	"	1·12	11	19	"	1·00
23	26	"	1·11	12	19	293	0·99
6	23	213	1·01	13	20	"	0·98
7	23	"	0·86	14	19	"	0·99
8	22	"	0·98	15	18	"	0·97
9	21	"	0·88				

For the reasons stated runs 11-15 were neglected and the remaining results given a least squares' treatment.

Result: $\frac{k_{Et}}{k_{pPr}} = 1·84 \pm 0·05 \exp(-279 \pm 12/RT)$

4·10. Topic No. 10 Fluorination of Ethane versus Methane.

Runs were carried out on mixtures of methane and ethane between +78° C and -75° C analysing for methyl and ethyl fluoride. Since CO_2 interfered in the analysis of the fluorides, nitrogen was used as the inert gas.

Chromatography:- Columns of 32' 20% nitrobenzene / firebrick (25-52 mesh) were used. A flow rate of 30cc/min eluted MeF in 5 min and EtF in 21 min.

Reactant Pressures:- The average pressures used in the reaction vessel were 1·5 mm fluorine, 4 cm hydrocarbon and 25 cm nitrogen giving F_2:hyd.:N_2 = 1·5:40:250. The results were not sufficiently accurate to observe any small inert gas pressure dependence.

The pressures of hydrocarbon were varied from ethane 2·36 cm, methane 1·93 cm (Run 14) to ethane 1·92 cm, methane 2·51 cm (Run 35) without effect. The average pressures used were ethane 2·02 cm and methane 2·10 cm.

The fluorine cell was replaced from run 27 onwards due to a fault in the old cell. The fluorine from the new cell contained an impurity and reacted very slowly (30 min had to be allowed for reaction). The impurity was probably oxygen which can be generated from electrolyte which has not undergone several amp. hrs.' generation. Perhaps this is the reason for the slow fluorination reaction of other workers[43].

However the results obtained were similar to those found with the purer fluorine and even seemed more concordant, probably because the reaction proceeded more slowly in more controlled conditions.

The results at room temperature were not in keeping with those at

other temperatures but when an outer jacket of cold water (at 20° C) was placed round the reaction vessel, they were in good agreement with the others. This would infer that the reaction was producing enough heat to raise the temperature of the reaction vessel to about 50° C (the results fitted the Arrhenius plot for 50° C). Although this explanation seems improbable, some heating effect may have occurred at +20° C and +78° C where the reaction proceeded faster due to more light being admitted to the uncovered reaction vessel and faster thermal generation of fluorine atoms. Also at higher temperatures the catalyzed decomposition of products may have a small effect. Both these factors would tend to lower the ratio EtF/MeF at those temperatures.

Where k_{Et} and k_{Me} are the rate constants of

$$F\cdot + CH_3CH_3 \longrightarrow HF + CH_3CH_2\cdot$$

and $$F\cdot + CH_4 \longrightarrow HF + CH_3\cdot$$

respectively, then

$$\frac{k_{Et}}{k_{Me}} = \frac{(EtF)}{(MeF)} \times \frac{(Me)}{(Et)}$$

The results are shown in Table 4·11 and the Arrhenius plot in Fig. 4·1.

Table 4·11 Results of Ethane / Methane Fluorination.

Run No.	Temp T °K	$\frac{k_{Et}}{k_{Me}}$	Run No.	Temp T °K	$\frac{k_{Et}}{k_{Me}}$
31	351	1·30	44	262	2·36
32	"	1·16	45	257	2·50
33	"	1·39	20	248	2·54
46	"	1·36	22	"	2·55
47	"	1·34	25	"	2·63
37	293	1·55	26	"	2·82
38	"	1·88	14	218	3·48
39	"	1·90	15	"	3·26
40	"	1·91	16	"	2·81
41	"	1·90	17	"	3·58
34	261	2·17	18	"	2·81
35	"	2·05	19	"	3·26
36	"	2·80	24	"	3·11
42	260	2·48	27	204	4·13
43	"	2·44	30	"	3·20
			48	198	3·39

Result from a least squares' treatment.

$$\frac{k_{Et}}{k_{Me}} = 0{\cdot}39 \pm 0{\cdot}04 \exp (928 \pm 41/RT).$$

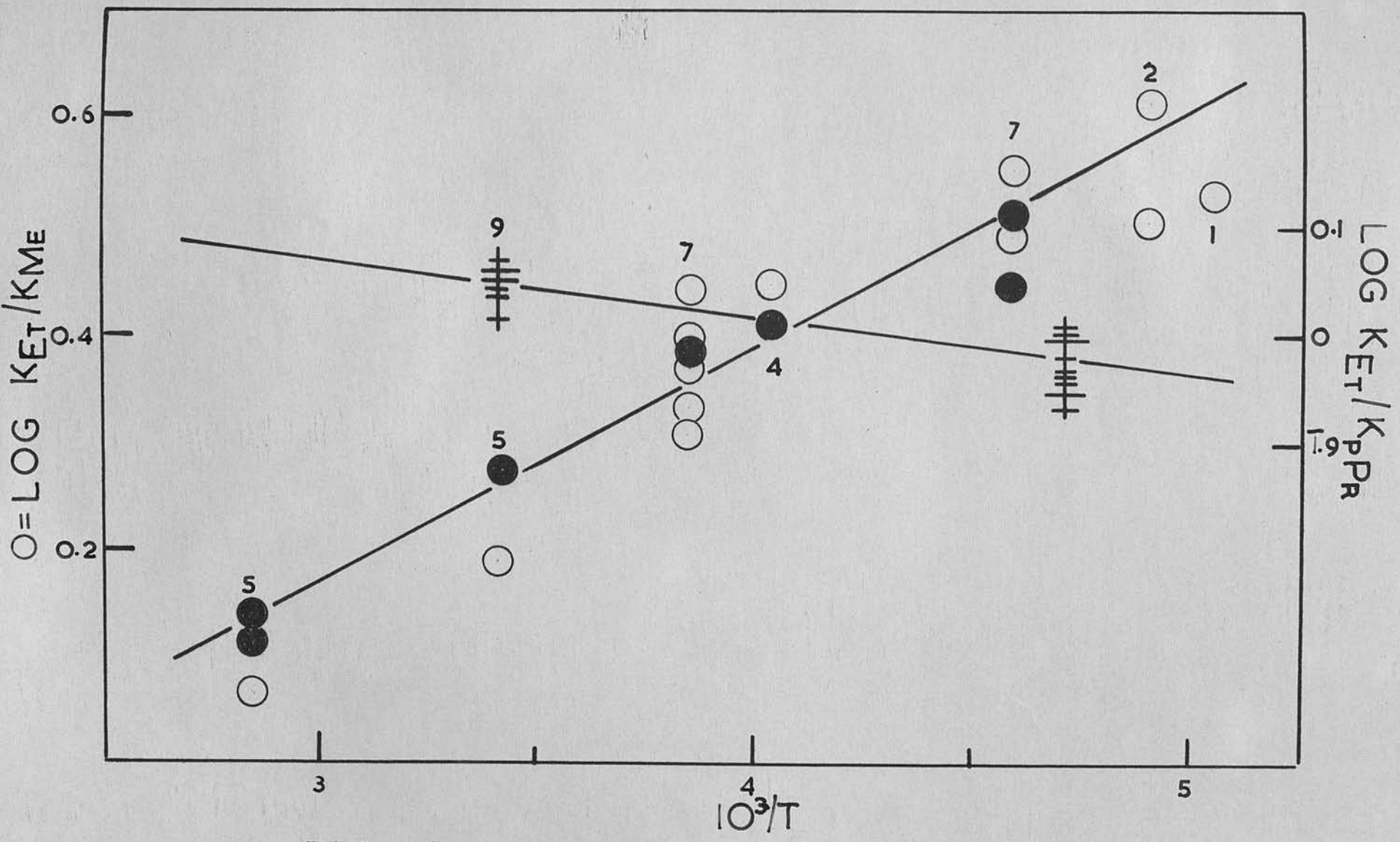


FIG. 4.1.

4·11. Calibration of Peak Areas.

Fluorides were trapped down as they eluted from the end of the chromatography columns after fluorinating the parent hydrocarbons (2·5 mm F_2 plus 8 cm hydrocarbon in the reaction vessel). The trapped fluorides were measured accurately on a gas burette, frozen back into the trap and fed back into the columns. In the cases of n-butane and propane both isomers were measured and the total area taken, i.e. it was assumed isomers would have similar sensitivities. Since the runs were carried out on two pairs of hydrocarbons using different conditions for each pair, only the results for the hydrocarbons within each pair can be compared.

Pair 1. Propyl Fluorides versus n-Butyl Fluorides.

Flow rate 35cc/min. Bridge Voltage ≏ 4 volts.

Gas	Total Volume μ moles	Total Peak Area @ 100% sensitivity	Area at 100% sens. per μ mole
Propyl fluorides	1·84	4·85 units	2·63 units
"	2·99	7·96	2·62
"	1·91	5·08	2·77
n-Butyl fluorides	3·73	9·62	2·58
"	2·97	7·81	2·63
"	2·28	6·00	2·63

Result:- The propyl and butyl fluorides have virtually identical sensitivities. Deviations which occur do not follow a trend and are probably experimental errors.

Pair 2. Ethyl Fluoride versus Methyl Fluoride.

Flow rate 30cc/min. Bridge Voltage ≏ 4 volts.

Gas	Total Volume µ moles	Total Peak Area @ 100% sensitivity	Area at 100% sens. per µ mole
Ethyl fluoride	3·07	9·53 units	3·11 units
"	2·97	9·48	3·19
Methyl fluoride	2·66	8·02	3·02
"	3·97	12·18	3·07

$$\frac{\text{Sens. EtF}}{\text{Sens. MeF}} = \frac{\text{Mean Area/µ mole EtF}}{\text{Mean Area/µ mole MeF}} = \frac{3{\cdot}15}{3{\cdot}05} = \frac{1{\cdot}03}{1}$$

Result:- Ethyl fluoride is 3% more sensitive than methyl fluoride.

Combining the two results, it is probable that a calibration factor is necessary only for methyl fluoride.

4.12. Unsuccessful Topics.

Ethane versus n-Butane:- Because of the difficulty found in separating ethyl fluoride, ethane and n-butane whilst still retaining good peaks for the butyl fluorides, the topic was abandoned.

Isobutane versus Propane:- The results were inaccurate due to the presence of secondary fluorination products within the isobutyl fluoride peak.

Methyl Chloride versus n-Butane:- Runs were carried out at 20° C and -60° C analysing for fluoro-chloro-methane and n-butyl fluoride. The columns and conditions were as for Topic 5. Analysis at 100% sensitivity had to be made for CH_2ClBr which eluted in 22 min. A small peak of impurity interfered and made the analysis inaccurate. The results were irreproducible, being 1.7 ± 0.3 at 20° C and 7 ± 1.5 at -60° C for the ratio $k_{pn\text{-}Bu}/k_{MeCl}$. This would correspond to $E_{MeCl} - E_{pn\text{-}Bu}$ = 2,100 cal., which seems rather high. A small activation energy probably does exist, however.

4·13. Accuracy of the Work.

Apart from those in Topics 9 and 10 the errors quoted on the results are the standard deviations (standard errors), σ, given by:

$$\sigma^2 = \frac{\Sigma v^2}{n-1}$$

where v is the deviation of each run from the arithmetic mean and n is the number of runs. The least squares' method which was used in Topics 9 and 10 was that given in Margenau and Murphy[68]. The errors quoted are the 50% probability limits. This probable error is equal to 0·6745 times the standard error for zero skew.

Systematic errors arising in pressure measurements were minimised by measuring gases in the same small volume at high pressures. Some loss of products in tap grease and differential pumping may have occurred. Peak area measurements were accurate to 1%. By using the competitive method these errors were reduced by cancellation. The main source of error was the temperature of the reactants. Where an activation energy was not apparent the temperature of the freezing mixtures probably deviated by $\pm 2^{\circ}$ C from the temperatures recorded. In Topics 9 and 10 an accuracy of $\pm 1^{\circ}$ C was obtained. However there was some indication that overheating of the reactants occurred. Sources of major error have been discussed in the individual topics.

CHAPTER 5.

THE REACTIONS OF BROMINE ATOMS.

5·1. Quantitative Kinetic Studies.

Quantitative kinetic studies of abstraction reactions by bromine atoms have been more detailed than in the case of fluorine. Because of this, in the following review of previous work no attempt has been made to describe reactions which have involved the addition of bromine atoms to an unsaturated system. The reactions described have been mainly confined to those involving the bromine abstraction of a hydrogen atom. Work in this field previous to 1954 has been reviewed in part by Steacie[69,70]. Cursory summaries of some of the later work[6,48] in addition to reviews of the earlier German investigations[71,72] have also appeared.

Hydrogen:-

The reaction between hydrogen and bromine to form hydrogen bromide has been extensively studied and is now one of the classics of chemical investigation. Bodenstein and Lind[73] followed the thermal reaction between 228-303° C. Reaction was carried out in sealed tubes, the final bromine and hydrogen bromide concentrations being measured by titration. The reaction was inhibited by HBr and within experimental error the inhibition was temperature independent. Their experimental results were represented by,

$$\frac{d(HBr)}{dt} = \frac{k\,(H_2)(Br_2)^{\frac{1}{2}}}{1 + \frac{(HBr)}{10(Br_2)}}$$

Christiansen, Herzfeld and Polanyi[74] accounted for this rate law by the

following mechanism

$$Br_2 \longrightarrow 2Br\cdot \quad (1)$$

$$Br\cdot + H_2 \longrightarrow HBr + H\cdot \quad (2)$$

$$H\cdot + Br_2 \longrightarrow HBr + Br\cdot \quad (3)$$

$$H\cdot + HBr \longrightarrow H_2 + Br\cdot \quad (4)$$

$$Br\cdot + Br\cdot \longrightarrow Br_2 \quad (5)$$

By steady-state treatment this gave,

$$\frac{d(HBr)}{dt} = \frac{2k_2\left(\frac{k_1}{k_5}\right)^{\frac{1}{2}}(H_2)(Br_2)}{1 + \frac{k_4}{k_3}\frac{(HBr)}{(Br_2)}}$$

Since k_1/k_5 is the equilibrium constant for the dissociation of bromine and k_4/k_3 was found experimentally to be 1/10, k_2 could be found. Also since k_4/k_3 is virtually temperature independent, the temperature dependence of the overall rate constant k leads to a value for the activation energy of reaction (2), E_2 from the relationship:

$$E = \tfrac{1}{2}\Delta H_1 + E_2$$

where E is the overall activation energy. Hence A_2 could be found. It is evident from the form of the kinetic equation that reaction (2) is the rate-determining step. This is supported by the thermochemistry of the system.

In later work Bodenstein and Jung[75] obtained values of k_3/k_4 from their investigation of the dark reaction at 300° ($k_3/k_4 = 8{\cdot}2$) and the light reaction at room temperature ($k_3/k_4 = 8{\cdot}6$). The mean value of $k_3/k_4 = 8{\cdot}4$ is usually accepted by most workers. $E_4 - E_3$ must then be small as must E_4 since E_3 on the thermochemical grounds is certainly small.

The thermal reaction was studied also by Bach, Bonhoeffer and Moelwyn-Hughes[76] over the range 276-313° C. Using the original value of $k_3/k_4 = 10$ their results gave only a slightly lower values of E_2 and A_2 then Bodenstein's. They also obtained values of E_2 and A_2 for deuterium which reacted more slowly

than hydrogen.

The photochemical reaction was studied by Bodenstein and Lütkemeyer[77] in a silica vessel over the range 160-218° C. The uptake of bromine was followed photometrically. The rate law was found to be independent of the total pressure. Jost and Jung[78] later investigated the effect of pressure between 4-400 mm and found the rate varied inversely as $\sqrt{P}$ where P is the total pressure. Jost[79] proved the effect of light in the band and continuous absorption regions of bromine had no effect. The excited bromine atom which is formed in the continuum must be deactivated by collision before reaction occurs. He explained the increase in rate observed with decrease of pressure by bromine atom recombination requiring three-body collision. He concluded that the effect of diffusion and recombination of bromine at the walls which occurred at low light intensities and pressures could be neglected for normal intensities and pressures. The rate law was then,

$$\frac{d(HBr)}{dt} = \frac{2k_2(H_2)\left[I_{abs}/k_5(M)\right]^{\frac{1}{2}}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}}$$

Since k_4/k_3, Iabs and k_5 were virtually temperature independent, the temperature dependence of the experimental overall rate constant gave E_2. A knowledge of the absolute rate constant k_2, obtained from the thermal reaction, is necessary to derive a value of A2 from the Arrhenius equation.

All these early workers however based their calculations on Bodenstein and Cramer's[80] dissociation constant of bromine. Pease[81] has recalculated them using Gordon and Barnes's[82] value. The results are shown in Table 9·12 along with various interpretations of other workers. Some reviewers have taken Bodenstein and Jung's values of k_3/k_4 as being slightly temperature dependent.

Both the thermal[83, 84] and photochemical[84] reactions were later studied briefly.

More recently, the thermal reaction has been studied at higher temperatures. Britton and Davidson[85] felt that their shock wave results on the hydrogen bromine flame reaction at 1396-1441° K offered some evidence that the Pease[81] equation would give considerable error on extrapolation. The shock wave results fitted better an equation of the form,

$$k = BT^h \exp(-H/RT)$$

suggested by Campbell and Fristrom[86]. These latter workers quoted a result obtained from the application of the numerical values listed by Pease[81] from Bodenstein and Lind's[73] results to this equation. This gave

$$k_2 = 3{\cdot}46 \times 10^{10} T \exp(-16{,}640/RT).$$

The work of Britton and Davidson[85] lead to a value of $5 < k_3/k_4 < 15$ for the higher temperatures.

However Levy[87] has studied the kinetics of the hydrogen bromine system by a flow method in the range 600-1400° K. The reaction was followed by separating bromine and HBr by distillation and measuring their volumes. Assuming the value of $k_3/k_4 = 8{\cdot}4$, he found his data could be represented by the equation analogous to Pease's,

$$k_2 = 2{\cdot}04 \times 10^{12} T^{\frac{1}{2}} \exp(-17{,}280/RT).$$

These later results are also included in Table 9·12.

Several workers have listed rate constants and Arrhenius parameters for the reactions involved in the hydrogen-bromine system. Unfortunately the papers of the original workers are not available and the method of calculation and experimental details (especially the mid-temperature) are uncertain.

Plooster and Garvin[88] have listed the results of Campbell and Hirschfelder as follows:

$$k_2 = 3{\cdot}46 \times 10^{10} T \exp(-16{,}640/RT)$$

This is the result quoted by Campbell and Fristrom[86] so presumably these workers'

results refer to the mid-temperature range of Bodenstein and Lind's[73] experiments (550°K). The values for the back reaction were calculated from the parameters of the forward reaction and presumably the equilibrium constant for (2) forward and (4) back to give:

$$k_4 = 7{\cdot}65 \times 10^{11} T^{\frac{1}{2}} \exp(-1100/RT)$$

From Bodenstein and Jungs'[75] results this gave

$$k_3 = 6{\cdot}42 \times 10^{12} T^{\frac{1}{2}} \exp(-1100/RT)$$

Cooley and Anderson[89] have reported the work of Anderson (the mid-temperature may again be 550° K). k_2 was probably taken from experiment and the others by calculation:

$$k_2 = 8{\cdot}05 \times 10^{10} T \exp(-17{,}700/RT)$$

$$k_3 = 2{\cdot}59 \times 10^{11} T \exp(-1100/RT)$$

$$k_4 = 3{\cdot}08 \times 10^{10} T \exp(-1100/RT).$$

A result is also given for:

$$Br_{\cdot} + HBr \longrightarrow H\cdot + Br_2 \qquad (6)$$

$$k_6 = 9{\cdot}31 \times 10^{10} T \exp(-41{,}700/RT).$$

The papers will have to be inspected before these values can be accepted. There seems to be some discrepancy between the values for the activation energies and the power to which the temperature term appears in the equations.

In view of the pressure dependence of the photochemical reaction, the reaction scheme suggested previously must be revised to give in the general case:[45]

$$Br_2 + h\nu \longrightarrow Br\cdot + Br\cdot \qquad (1)\ \text{photochemical or}$$

$$Br_2 + M \longrightarrow Br\cdot + Br\cdot + M \qquad (1a)\ \text{thermal}$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot \quad (2)$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \quad (3)$$

$$R\cdot + HBr \longrightarrow RH + Br\cdot \quad (4)$$

$$Br\cdot + Br\cdot + M \longrightarrow Br_2 + M \quad (5)$$

Where R· is normally a hydrogen atom or substituted alkyl group. M might be expected to be equally efficient in (1a) and (5) so the thermal reaction would be pressure independent as is found by experiment.

The earlier work on hydrogen was followed by a succession of papers on the bromination of hydrocarbons, the homologous series of alkanes receiving the most attention.

Methane:-

Kistiakowsky and Van Artsdalen[84] studied the photobromination of methane over the temperature range 150-230° C. The products were mainly HBr and methyl bromide. Secondary bromination could be neglected. The rate of reaction was followed by measuring the uptake of bromine with time photometrically. Extrapolation was made to give the rates at zero time, so that the effect of products formed during the reaction was at a minimum. HBr and oxygen inhibited the reaction. The inhibition of the former was temperature dependent. The rate law which was found to hold over a three-fold variation in methane, bromine and total pressures was,

$$-d(Br_2)/dt = k\,(CH_4)(Br_2)^{\frac{1}{2}}(1/P)^{\frac{1}{2}}.$$

In the presence of HBr a term $\left[1 + k_4(HBr)/k_3(Br_2)\right]$ appeared on the denominator. This is exactly the same as the hydrogen case and the same mechanism must apply. The temperature-dependence of k , the overall rate constant, gave E_2, the activation energy of the rate-controlling step. Using values of k obtained from the rate law in the absence of HBr, k_4/k_3 was found over the range 37-210° C

and from the Arrhenius plot E_4-E_3 and A_4/A_3 were found. E_3 was assumed to be zero since reaction (3) is an exothermic radical process.

The thermal reaction was also studied at 297° C. The experimental rate law agreed with the hydrogen case in the absence of HBr. The absolute value of k_2 obtained was used in conjunction with the photochemical activation energy to give A_2.

Results:

E_2 = 18·25 kcal. A_2 = $5·89 \times 10^{13}$ cc mole^{-1}sec^{-1}

$E_4-E_3 \sim E_4$ = 2 kcal. A_4/A_3 = 0·2.

Methyl Bromide:-

This was studied photochemically[84] in exactly the same way as methane over the range 150-230° C. No inhibition by HBr was found. The mechanism proposed was as before, except that E_4 was thought to be large and reaction (4) negligible. The thermal reaction was carried out under the same conditions as for methane. Values for E_2 and A_2 were obtained.

Results:

E_2 = 16·05 kcal A_2 = $5·32 \times 10^{13}$ cc mole^{-1}sec^{-1}.

The method of Kistiakowsky and Van Artsdalen was subsequently used in the following cases by Van Artsdalen and co-workers. The rate laws were the same unless where mentioned.

Ethane:-

The photochemical bromination of ethane[90] was followed between 35° and 90° C. Ethyl bromide and HBr were virtually the only products over the first 10% of reaction. HBr inhibited the reaction and the inhibition was temperature

independent. A rate law similar to methane was put forward which however did not fit the results exactly since k decreased with decreasing ethane pressure and increased with decreasing bromine pressure. Attempts were made to correct for this by introducing terms into the rate law for heterogeneous recombination of bromine atoms and varying efficiencies of M in reaction (5). This led to variations of a factor of three in the rate constants but affected the activation energy E_2 very little. As before temperature inhibition data gave k_4/k_3 which was temperature independent and so $E_4 \sim E_3$. E_3 was assumed to be small. E_4 must then be small. No thermal bromination was attempted so no value of A_2 was obtained.

Results:

E_2 = 13·9 kcal $\qquad$ $E_4 - E_3$ = 0

A_4/A_3 = 0·6 $\qquad$ E_4 assumed to be <2 and probably 0·8 kcal.

Neopentane:-

The photochemical bromination[91] was followed over the range 98-152° C. HBr inhibited the reaction to a greater extent than in the methane case. The inhibition was temperature dependent. Water and oxygen were also inhibitors. The experimental rate law

$$-d(Br_2)/dt = k'(Br_2)^{\frac{1}{2}}(\text{Neopentane})$$

was found to be obeyed equally as well as the one generally found before over a threefold variation in (Br_2) and (Neopentane). This was attributed to the latter being present in greater amount than the former and to neopentane being a more efficient third body. In other work[83] the photochemical reaction was studied between 124-181° C. From ratios of the rates at 471° K compared with the rates for hydrogen, neopentane was found rather unreasonably to be 175 times more efficient than hydrogen as a third body. The overall temperature-dependence gave the same

value of E_2 in both cases. Rather scattered inhibition data in the former work gave E_4-E_3 and A_4/A_3. E_3 was assumed to be small. The thermal reaction was studied at 197° C to give A_2.

Results:

$E_2 = 18{\cdot}1$ kcal $\qquad A_2 = 9{\cdot}3 \times 10^{16}$ cc mole^{-1} sec^{-1}

$E_4-E_3 \sim E_4 \simeq 9{\cdot}9$ kcal $\qquad A_4/A_3 \simeq 10^{5{\cdot}8}$.

Toluene:

The photobromination[92] was followed over the range 82-132° C. I.R. analysis showed the products were almost exclusively benzyl bromide and HBr arising from attack at the side chain. The reaction was strongly inhibited by HBr and also by oxygen. The inhibition by HBr was temperature dependent. The rate law,

$$-d(Br_2)/dt = k'(Br_2)^{\frac{1}{2}}(RH)^{\frac{1}{2}}$$

in the absence of HBr fitted the results better than the usual law for the same reason, it was thought, as in the neopentane case. Scattered inhibition data gave A_4/A_3 and E_4-E_3. E_3 was assumed to be small. A very brief investigation of the thermal bromination at 166° C gave A_2.

Results:

$E_2 = 7{\cdot}6$ kcal $\qquad A_2 = 3\ 3 \times 10^{13}$ cc mole^{-1} sec^{-1}

$E_4-E_3 \sim E_4 \simeq 5{\cdot}0$ kcal $\qquad A_4/A_3 \simeq 10^{3{\cdot}0}$.

Isobutane:-

The photochemical bromination[93] was followed over the range 40-95° C. tert. Butyl bromide was the only monobromide detected. The reaction was inhibited by HBr and oxygen. HBr inhibition was temperature-dependent. The usual parameters were evaluated. The thermal reaction was followed briefly at both 112° and 130° C. The photochemically derived activation energy was used to obtain A_2.

Results:

E_2(photochemical) = 11·7 kcal E_2(thermal) = 12·5 kcal

$E_4-E_3 \sim E_4 \simeq 8{\cdot}0$ kcal $A_2 = 3{\cdot}8 \times 10^{17}$ cc mole^{-1} sec^{-1}

$A_4/A_3 \simeq 10^{5{\cdot}1}$.

The later bromination work has come under criticism from its reviewers[6,48,70,94]. The main points of criticism were:

(1) In the cases of isobutane and neopentane A_2 was far too high since it was much greater than the collision frequency. The inhibition work was inaccurate and the value of A_4/A_3 was thought to be unlikely. The large value of E_2 relative to ethane was partially offset by a high value of E_4-E_3.

(2) The values of k_4/k_3 for toluene passed through unity despite E_4-E_3 = 5 kcal. The value of the ϕCH_2-H bond strength derived from the activation energy work (89·5 kcal) differed from Szware's[95] figure of 77·5 kcal which is supported by electron impact work. The value of A_4/A_3 was again thought to be unlikely.

Benson and Graff[96] attempted to explain the high value of A_2 for neopentane by suggesting the possibility of decomposition of the intermediate neopentyl radical. They put forward the scheme:

$Br\cdot + N_pH \longrightarrow N_p\cdot + HBr$ (2)

$N_p\cdot \longrightarrow$ isobutene + $CH_3\cdot$ (7)

$CH_3 + N_pH \longrightarrow CH_4 + N_p\cdot$ (8)

$CH_3 + Br_2 \longrightarrow CH_3Br + Br\cdot$ (9)

isobutene + $Br\cdot \longrightarrow$ Br-isobutyl (10)

Br-isobutyl + $Br_2 \longrightarrow$ di Br-isobutane + Br (11)

Reaction (7) was expected to have an activation energy of 23 kcal and an A factor of $\sim 10^{13}$ sec^{-1} was assumed. With these parameters (7) could compete with other reactions of the N_p radical to give $E_2 = 12 \pm 2$ kcal and $A_2 = 10^{14}$ cc mole^{-1} sec^{-1}. However no such explanation could be put forward for

isobutane and at the bromination temperatures radical decomposition should be unimportant compared with combination.

In a later paper Benson and Buss[97] calculated the time to reach a fraction of the stationary-state conditions of X· from independent measurements of the rates of

$$X\cdot + X\cdot + M \longrightarrow X_2 + M.$$

They found that for bromine atoms the time for the thermal reaction at 480° C to reach 90% of the stationary-state would be 100 sec if homogeneous initiation and termination of the chains occurred. If atoms were formed at the walls and chains started and stopped at the walls, the gas phase concentration of bromine atoms would be less than that expected from the dissociation equilibrium constant unless diffusion and, or convection were much faster than evaporation and condensation of atoms at the walls. In either case, they concluded, it was almost certain that RH + Br· would react at the walls in measurable amounts. Therefore if the rate of reaction was fast, i.e. the time of a run was short compared with the induction period, heterogeneous reaction would be appreciable. From a consideration of chain lengths this appeared to be the case in some of the brominations. Even in the photochemical work in those cases the induction period was not too small to be neglected.

They also considered the possibility of several chain terminating steps:

$$2X\cdot + M \xrightarrow{k_{2X}} X_2 + M \qquad (12)$$

$$X\cdot + R\cdot\,(+M?) \xrightarrow{k_{XR}} RX \qquad (13)$$

$$R\cdot + R\cdot\,(+M?) \xrightarrow{k_{2R}} R_2 \qquad (14)$$

Using experimentally and thermodynamically derived rate constants values of Θ were obtained from the relationship,

$$R/X = \theta = (k_2/k_4)(k_4/k_3)(RH/X_2)$$

where the k's are the rate constants of the reactions in the general scheme given before. From the equations,

$$\frac{\text{Rate (13)}}{\text{Rate (12)}} = \frac{k_{XR}}{k_{2X}}\theta \qquad \text{and} \qquad \frac{\text{Rate (14)}}{\text{Rate (12)}} = \frac{k_{2R}}{k_{2X}}\theta^2,$$

using guessed values of k_{2R} and k_{XR} in conjunction with found values of k_{2X} and θ, the relative importance of reactions (13) and (14) compared to (12) could be assessed to see if they were consistent with the experimental rate laws.

They concluded that the work on hydrogen, methane and methyl bromide was satisfactory. In the ethane case recombination by $C_2H_5\cdot$ + Br· must have occurred. The effects found for isobutane and neopentane were more pronounced. The induction periods for the thermal reactions were appreciable and the chain lengths long, so heterogeneous reaction had occurred. Also recombination by R· + R· and R· + Br· was more important than by R· + X·. Some heterogeneity must also have occurred in the photochemical work since the induction periods were appreciable. The length of the thermal induction period and radical recombination mainly by (13) and (14) were also sources of error in the toluene work. The photochemical rate constant appeared lower than expected from quantum yield considerations, so either it was wrong or the investigations were carried out in non-stationary state conditions. It was therefore thought that only the values of E_2 could be accepted for toluene, isobutane and neopentane, and even these with some doubt.

Chloroform:-

The bromination of chloroform has been studied by several workers. The earliest photochemical work was by Willard and Daniels[98] on liquid chloroform and yielded only qualitative results.

Braunwarth and Schumacher[99] studied the photochemical vapour phase

reaction at 110° and 130° C. The uptake of bromine was followed photometrically and checked by titration. The effects of variations in the pressures of chloroform, bromine, HBr and added nitrogen were investigated. They found that below 90 mm wall recombination of bromine atoms occurred. This leads to the rate law in the absence of CCl_3Br which inhibited the reaction:

$$\frac{-d(Br_2)}{dt} = \frac{kIabs(CHCl_3)P}{1 + k_4(HBr)/k_3(Br_2)}$$

A similar effect was found by Jost[79] for hydrogen. Above 200 mm chain ending was almost exclusively by three-body recombination of bromine atoms and the more usual rate law found, e.g. for methane, was obeyed. HBr was found to inhibit the reaction. The temperature coefficient for the inhibition was very small. The mechanism proposed was similar to that given for the general case (p. 83) except that the reaction,

$$CCl_3Br + Br^{\cdot} \longrightarrow CCl_3^{\cdot} + Br_2 \qquad (15)$$

had to be included in the scheme to account for the inhibition by CCl_3Br and reversibility of the reaction. Since the temperature coefficient of k_4/k_3 was practically zero.

$$E_4 - E_3 \sim 0$$

The temperature coefficient of the overall reaction gave E_2. From a study of the bromine sensitized photochemical oxidation of trichloro-bromo-methane Franke and Schumacher[100] estimated values for E_3 and E_{15}.

Results:

$E_2 = 10 \pm 1$ kcal $\qquad E_3 = 6\text{-}7$ kcal

$E_4 = 6\text{-}7$ kcal $\qquad E_{15} = 6$ kcal

$A_4/A_3 = 0{\cdot}14$

Sullivan and Davidson[101] later studied the kinetics of both the forward and back thermal reaction of chloroform in the range 420-455° C. The reaction was carried out in sealed vessels and the final bromine volume measured

by titration. The overall experimental rate law was,

$$\frac{-d(Br_2)}{dt} = \frac{k_f(CHCl_3)(Br_2)^{\frac{1}{2}}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}} - \frac{k_r(CBrCl_3)(Br_2)^{\frac{1}{2}}}{1 + \frac{k_3(Br_2)}{k_4(HBr)}}$$

where k_f and k_r are the overall rate constants for the forward and back reactions respectively. The mechanism proposed was the same as by Schumacher, again with the inclusion of reaction (15) which was responsible for the reverse reaction. k_4/k_3 was measured with good agreement both from a study of the inhibited forward reaction, as well as the back reaction and a consideration of the equilibrium constant. k_4/k_3 was temperature independent. Reactions (3) and (15) provided a mechanism for the exchange of labelled bromine between trichlorobromomethane and bromine. The rates obtained were similar to those obtained for the exchange rate constants by the same workers[102], thus demonstration that reactions (3) and (15) were indeed the path for the exchange. The overall rate constants lead to Arrhenius parameters for reactions (2) and (15), both since $k_2 = k_f K^{-\frac{1}{2}}$ and $k_{15} = k_r K^{-\frac{1}{2}}$, where K as before is the equilibrium constant for bromine.

Results:

$E_2 = 9{\cdot}3$ kcal
$A_2 = 2{\cdot}29 \times 10^{12}$ cc mole^{-1} sec^{-1}
$A_4/A_3 = 0{\cdot}04$

$E_{15} = 10{\cdot}2$ kcal
$A_{15} = 8{\cdot}1 \times 10^{13}$ cc mole^{-1} sec^{-1}
$E_4 - E_3 = 0 \pm 1$ kcal
$E_4 \leq 7$ kcal

Although the value of E_2 compares with that of Braunwarth and Schumacher,[99] k_4/k_3 does not. The values of E_3 and E_{15} estimated by Franke and Schumacher would lead to the value of $\Delta H = 4$ kcal for

$$CHCl_3 + Br_2 \longrightarrow CBrCl_3 + HBr$$

This would imply that the equilibrium lies well to the left which is not the case since Davidson and Sullivan found K tended to a value of 2.

Chloral:-

Klug and Schumacher[103] investigated the photobromination of chloral in the range 70-90° C. The quantum yield under their conditions was ~ 120. Unlike the corresponding chlorination the reaction was complex, since not only were CCl_3Br and CO formed from the overall reaction,

$$CCl_3CHO + Br_2 \longrightarrow CCl_3Br + CO + HBr \qquad (16)$$

but also some $COBr_2$ and $CHCl_3$ from the reactions,

$$CCl_3CHO + 2Br_2 \longrightarrow CCl_3Br + HBr + COBr_2 \qquad (17)$$

and $$CCl_3CHO + Br_2 \longrightarrow CHCl_3 + CO + Br_2 \qquad (18)$$

The rate of formation of CO was proportional to $\sqrt{I_{abs}}$ and approximately to (CCl_3CHO), the rate being a maximum for a 1:1 mixture of bromine and chloral. The reaction was not affected by pressure changes but was sensitive to surface conditions. While neither HBr nor CCl_3Br were inhibitors, the other products, along with especially trichloroacetyl bromide, did have a retarding effect. In view of these facts the mechanism tentatively proposed was:

$$Br_2 + h\nu \longrightarrow Br\cdot + Br\cdot \qquad (1)$$

$$Br\cdot + CCl_3CHO \longrightarrow CCl_3CO\cdot + HBr \qquad (2)$$

$$CCl_3CO\cdot + HBr \longrightarrow CHCl_3 + CO + Br\cdot \qquad (19)$$

$$CCl_3CO\cdot + CCl_3CHO \longrightarrow CHCl_3 + 2CO + CCl_3\cdot \qquad (20)$$

$$CCl_3CO\cdot + Br_2 \longrightarrow COBr_2 + CCl_3\cdot \qquad (21)$$

$$CCl_3\cdot + Br_2 \longrightarrow CCl_3Br + Br\cdot \qquad (22)$$

$$CCl_3Br + Br\cdot \longrightarrow CCl_3\cdot + Br_2 \qquad (23)$$

$$CHCl_3 + Br\cdot \longrightarrow CCl_3\cdot + HBr \qquad (24)$$

$$CCl_3\cdot + HBr \longrightarrow CHCl_3 + Br\cdot \qquad (25)$$

$$2CCl_3CO\cdot \longrightarrow C_2Cl_6 + 2CO \qquad (26)$$

For the beginning of the reaction when $(CHCl_3) \sim (CCl_3Br) \sim (HBr) = 0$ the rate law for the formation of CO derived from a consideration of reactions (1), (2), (20), (21), (22) and (26) was:

$$d(CO)/dt = 2k_{20}\sqrt{I_{abs}/k_{26}}(CCl_3CHO),$$

in agreement with experiment. The overall activation energy gave $E_{20} - \frac{1}{2}E_{26}$ = 11 kcal. E_{26} was thought to be small. Schumacher[71] has listed a value for E_2 from a consideration of this work. A value of $E_2 = 8 \pm 3$ kcal was also suggested by Stauff and Schumacher[104] from their work on the bromine-sensitized photooxidation of chloral. Schumacher suggested the distinct difference between the photobromination and chlorination of chloral was due to the possibility that while reaction (27) occurs

$$CCl_3CO + Cl_2 \longrightarrow CCl_4 + CO + Cl\cdot \qquad (27)$$

readily ($E_{27} \sim 6$ kcal), it does not occur with bromine. E_{27} was suggested to be 16 kcal for bromination.

Results:

$E_{20} = 12 \pm 2$ kcal $\qquad E_2$ (a) < 8 kcal (b) 8 ± 3 kcal.

Benzene:-

Meidinger[105] studied the photobromination of benzene in the liquid phase and in carbon tetrachloride solution over the range 20-56° C. The bromine uptake was measured photometrically. The rate of reaction was dependent upon the light intensity and the concentration of hydrogen bromide and benzene present but was independent of wavelength and bromine concentration. Addition of bromine to the benzene ring competed with the substitution reaction. The ratio $k_{addition}/k_{substitution}$ varied directly as $\sqrt{I}$ and inversely partially as $(C_6H_6)^{\frac{1}{2}}$. Both reactions were thought to go by a radical mechanism similar to the other cases described here. The temperature coefficient reported was 1·6 for ~ 30° C range which, however, fell to 1·0 with dilution.

The results of Rabinowitsch[106] who studied the same reaction under similar conditions agreed, qualitatively at least, with Meidinger's results. However

the addition reaction was postulated to go by a molecular mechanism. Bromine molecules were thought to remain attached to benzene even when diluted by solvent. In the formation of the addition compound bromine molecules activated by the light reacted with the benzene ring. Substitution was however a radical process. The fall off in temperature coefficient reported by Meidinger was attributed to the effect of carbon tetrachloride solvation on the bromine molecule. This effect has been discussed by Young and Style[107]. Although the bromine becomes less photosensitive the rate of reaction can be much greater than would be expected if the Arrhenius thermal activation energy were the sole controlling factor. The addition reaction was less sensitive to dilution than the substitution. The high temperature coefficient was attributed to a high thermal activation energy for the substitution and was probably for the step,

$$C_6H_6 + Br\cdot \longrightarrow C_6H_5\cdot + HBr \qquad (28)$$

Result:

$$E_{28} \simeq 7 \text{ kcal.}$$

Naphthalene:-

Sixma and Wibaut[108] investigated the thermal bromination of gaseous naphthalene. At lower temperatures substitution occurred by an ionic mechanism. Radical reaction only occurred at elevated temperatures, presumably by the usual mechanism. The activation energy of (29)

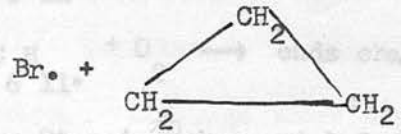
$$Br\cdot + \alpha C_{10}H_8 \longrightarrow HBr + \alpha C_{10}H_7\cdot \qquad (29)$$

was assumed to be between 0-5 kcal.

Cyclopropane:-

The photobromination of gaseous cyclopropane appears to result almost exclusively in opening of the ring according to the work of Ogg and Priest[109,110] who reported that the principal product was 1,3-dibromopropane. The first step was

the reaction,



$$Br\cdot + \text{(cyclopropane)} \longrightarrow BrCH_2CH_2CH_2\cdot \qquad (30)$$

Only 2% HBr was formed. E_{30} was $\ll 17.3$ kcal. However it is interesting to note that in their brief study[110] of the dark reaction at 220° C large amounts of HBr were formed, suggesting the possibility of substitution.

The work of Kharasch[111] in solution at 20° gave similar products to those found by Ogg and Priest photochemically.

Cyclohexane:-

The photochemical vapour phase bromination of cyclohexane was studied by Pusch[112], Noddack[113], Wood and Rideal[114] and Jost[115]. Pusch and Noddack employed radiation corresponding to the continuous and did not take precautions to exclude oxygen. Their quantum yield was one. Wood and Rideal used a glass apparatus at room temperature with radiation corresponding to the band absorption. A slow dark reaction was reported to occur. The reaction products consisted mostly of the di- and tri-bromo cyclohexanes.

Jost worked in a quartz apparatus at 73-106° C. Since he found no dark reaction occurred, he attributed the result of Wood and Rideal to wall reaction. The reaction was independent of wavelength. Both Wood and Rideal and Jost agreed that the rate was proportional to Iabs and was inhibited by oxygen. Jost also found the rate was approximately proportional to $(\text{cyclohexane})^{\frac{1}{2}}$. In the absence of oxygen quantum yields varied from 12 to 37. The result of 3 to 7 in its presence agreed with the work of Pusch and Noddack. Jost suggested the mechanism:

$$Br_2 + h\nu \longrightarrow Br\cdot + Br\cdot \qquad (1)$$

$$Br\cdot + C_6H_{12} \longrightarrow C_6H_{11}\cdot + HBr \qquad (31)$$

$$C_6H_{11}\cdot + Br_2 \longrightarrow C_6H_{11}Br + Br\cdot \qquad (32)$$

$$C_6H_{11}\cdot + O_2 \longrightarrow \text{ends chain} \qquad (33)$$

However Steacie[70] has pointed out that the reaction was not as strongly dependent upon the bromine concentration as this mechanism would suggest from the resulting law which was:

$$\frac{-d(Br_2)}{dt} = \frac{kIabs(Br_2)}{(O_2)}.$$

He suggested that the rate law resulting from substitution of (33) by reaction (34) should be combined with Jost's mechanism to fit the experimental facts.

$$Br\cdot + \text{wall} \longrightarrow \tfrac{1}{2}Br_2 \qquad (34)$$

The law was:

$$-d(Br_2)/dt = kIabs(C_6H_{12}).$$

Jost reported a temperature coefficient of 2 for the 30° C range. This would correspond to an activation energy of ~8.5 kcal due probably to reaction (31).

Butane Derivatives:-

The results of Tedder and co-workers have already been described in Chapter 2·2. Unfortunately no temperature coefficients were obtained.

5·2. Qualitative Work.

Qualitative bromination investigations have been carried out mainly in solution. Although these experiments do not lead to any definite kinetic parameters they do give information on the products formed by higher bromine conversions, as well as some possible differences of solution and gas phase media.

Kharasch, White and Mayo[116] investigated the effect of conditions on the liquid phase bromination of toluene. Oxygen, peroxides, illumination, heat and dilution with solvent favoured the side chain radical attack in competition with polar ring reaction. Some organic material e.g. nitro compounds inhibited the reaction.

Continuing research on the effect of conditions Kharasch, Hered and Mayo[117] carried out further liquid phase work. At 25-30° C isobutane yielded 60% t-butyl bromide and 40% dibromide of structure $CH_2Br\text{-}\overset{CH_3}{\overset{|}{C}}Br\text{-}CH_3$. Cyclohexane yielded only cyclohexyl bromide but methyl cyclohexane gave 75% mono- and 25% dibromide. The photochemical reaction was slower at higher bromine concentrations. The reactions including that with toluene were retarded by excess oxygen. However even with excess oxygen the reaction was much faster than in its total absence. This is in marked contrast to the vapour phase work.

Since the early work indicated that at room temperature compounds containing tertiary and secondary hydrogens reacted readily in the order tertiary > secondary, neopentane was brominated because it contained only primary bonds. In the gas phase at higher temperatures mixtures of normal and secondary products were formed in the work of Perelis[118]. However Kharasch and Fineman[119] found that the primaries in neopentane and also in trimethyl acetic acid and t-butyl benzene were not attacked noticeably in the liquid phase at 80° C. Neopentane was only attacked appreciably photochemically if traces of oxygen were present.

The following mechanism for neopentane was suggested which could explain the oxygen effect for all the solution work:

$$(CH_3)_4C + O_2 \xrightarrow{h\nu} (CH_3)_3CCH_2\cdot + HO_2\cdot \quad (35)$$

$$HBr + O_2 \longrightarrow HO_2\cdot + Br\cdot \quad (36)$$

$$(CH_3)_3CCH_3 + Br\cdot \longrightarrow HBr + (CH_3)_3CCH_2\cdot \quad (37)$$

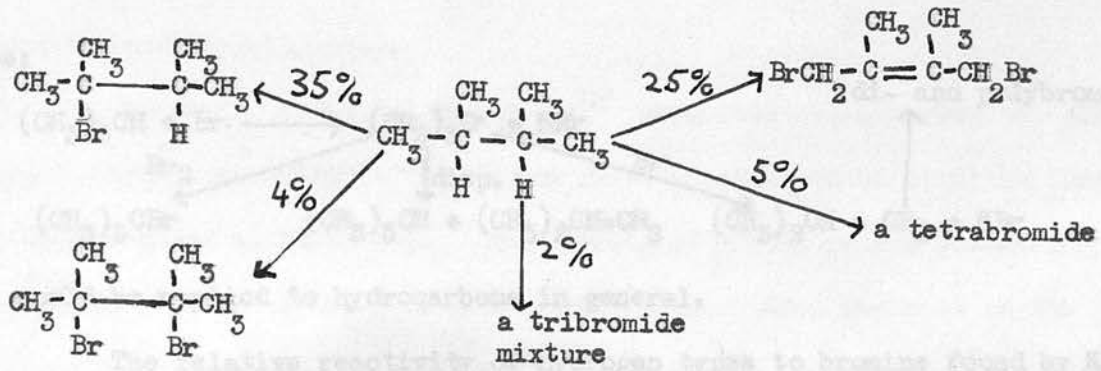
$$(CH_3)_3CCH_2\cdot + Br_2 \longrightarrow (CH_3)_3CCH_2Br + Br\cdot \quad (38)$$

It could be argued that traces of oxygen did not inhibit reaction in solution in contrast to the gas phase because the kinetic chains in solution were relatively short. Under these conditions, bromine atoms which are oxygen inert would be the chief species present, since hydrogen abstraction was the slow step. Oxygen might even protect the atoms from chain-ending attack. Inhibition by higher pressures of oxygen could be explained by competition of the oxygen with the bromine molecules for hydrocarbon radicals. In the gas phase this would always be the controlling reaction under the kinetic conditions so that oxygen would always be an inhibitor even in trace amounts.

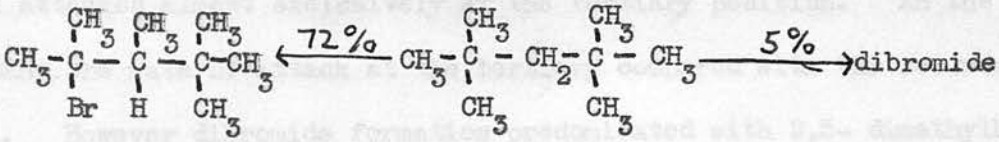
n-Pentane was reported by Kharasch, Zimmt and Nudenberg[120] to react only slowly when brominated photochemically at 80° C. Because the products found were a mixture of amyl bromides (probably from attack at the secondary positions) no disintegration of the n-pentane molecule had occurred, which refuted the work of Williams and Hamill[121].

From their work on aliphatic acids Kharasch and Hobbs[122] concluded that while n-butyric and propionic acids brominated by a radical chain mechanism, acetic acid did not.

Kharasch, Liu and Nudenberg[123] studied the vapour phase photobromination of higher branched hydrocarbons. At 100° C 2,3-dimethylbutane gave the products shown below:



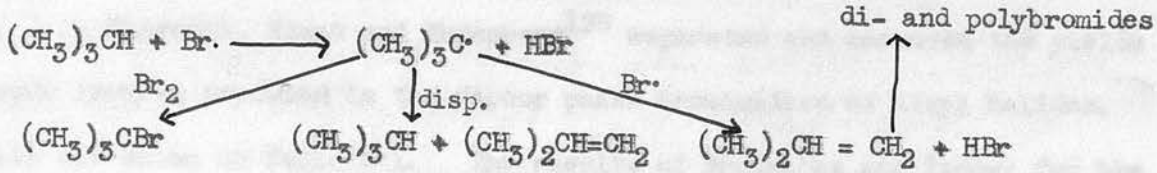
A higher temperature of 200° C was required for reaction with 2,2,4,4 - tetramethyl pentane which gave,



The formation of the monobromide from 2,3- dimethylbutane was thought to go by the usual chain mechanism. However the monobromide formed from the branched pentane involved the rearrangement of a methyl group. It was suggested that rearrangement of the radical formed by the abstraction of a secondary hydrogen atom by a bromine atom occurred.

The method of formation of the polybromides was uncertain. Earlier workers[124] reported that the liquid phase bromination of 2,3- dimethylbutane yielded only 2,3- dibromo- 2,3- dimethylbutane. They attributed this to the monobromide first formed being more susceptible to bromination than the parent hydrocarbon. Kharasch and co-workers thought the difference of products found in their vapour phase work was due to the conditions prevailing in solution. Products formed in solution appear to be strongly dependent on bromine concentration, temperature, light and impurities. They decided therefore that while it could not be denied that dibromides could arise by the further bromination mechanism in solution, at the bromine concentrations found in the vapour phase some other mechanism must occur. They supported the formation of an olefin as an intermediate, not from a dehydrohalogenation reaction postulated previously[117], but by the following

steps:



This could be applied to hydrocarbons in general.

The relative reactivity of hydrogen types to bromine found by Kharasch and co-workers was supported by Russel and Brown[125] who found tertiary > secondary > primary in reactivity. At 25° C in the liquid phase cumene and 2,2,3- trimethylbutane were attacked almost exclusively at the tertiary position. In the case of 2-methyl pentane the rate of attack at the tertiary compared with the secondary was at least 36:1. However dibromide formation predominated with 2,3- dimethylbutane in agreement with the previous solution work and again differing from Kharasch's vapour phase work. The amount of dibromide fell at lower temperatures (0° C) and lower bromine-hydrocarbon ratios. Because of this, they refuted (as did Kharasch) the mechanism involving bromination of the supposedly more reactive monobromide (Fredricks and Tedder[38] found in the gas phase attack at the α - position to the halogen present in n-butane was faster and at the β slower than in the parent hydrocarbon) on the grounds that the amount of dibromide should increase at low temperatures where increased selectivity would occur. Thermal bromination of the monobromides themselves in the presence of peroxide proved slower than in its absence. They decided that dibromide formation in the photobromination of branched chain hydrocarbons in solution was due to an ionic or molecular attack of bromine on the monobromide which was first formed presumably by the usual chain mechanism. The possibility of olefin formation by elimination of HBr from the intermediate ion in the second step was thought to be unlikely. Their results showed that the ease of dibromide formation increased with the nature of the hydrogen atom in the position adjacent to the halogen already present in the order

primary < secondary < tertiary.

Kharasch, Zimmt and Nudenberg[126] separated and measured the yields of bromo isomers produced in the vapour phase bromination of alkyl halides. Their results are shown in Table 5·1. The results of Fredricks and Tedder for the bromination of n-butyl chloride are in agreement. Also included in the table are the results of McBee and co-workers[127] obtained from the vapour phase thermal bromination of fluorinated alkanes at 500° C. This work was carried out to prepare new bromo-fluoro-compounds. Other side products were formed. However some qualitative information about the relative rates of attack of bromine at different positions in perhalogenated alkanes may be obtained.

Table 5·1. Products from Bromination of Alkyl Halides.

Compound		Products	%	Conditions	Reference
$CH_3CH_2CH_2CH_2Br$		$CH_3CH_2CHBr.CH_2Br$	30	100° C; gas phase;	126
		$CH_3CHBr.CH_2CH_2Br$	13	photochemical	
		$C_4H_7Br_3$	30		
		$CH_2Br.CHBr.CHBr.CH_2Br$	10		
$CH_3CH_2CHBrCH_3$		$CH_3CH_2CBr_2CH_3$	19		
	meso	$CH_3CHBr.CHBr.CH_3$	22	"	"
	racemic	"	10		
		$C_4H_7Br_3$	34		
		$CH_2Br.CHBr.CHBr.CH_2Br$	6		
$CH_3CH_2CH_2CH_2Cl$		$CH_3CH_2CH_2CHClBr$	23		
		$CH_3CH_2CHBr.CH_2Cl$	23	"	"
		$CH_3CHBr.CH_2CH_2Cl$	46		
$CH_3CH_2CHClCH_3$		$CH_3CH_2CClBr.CH_3$	80	"	"
$CH_3CH_2CH_2Br$		$CH_3CHBr.CH_2Br$	71		
		$CH_2BrCHBr.CH_2Br$	18	"	"
$CH_3CHBrCH_3$		$CH_3CBr_2.CH_3$	85	"	"
$CH_3CH_2CH_2Cl$		$CH_3CH_2CHClBr$	45		
		$CH_3CHBr.CH_2Cl$	45	"	"

Table 5·1. (continued).

Compound	Products	%	Conditions	Reference
CH_3CH_2Br	CH_3CHBr_2	86	198° C; gas phase; photochemical;	126
$CH_3CH_2CH_2CH_2Cl$	$CH_3CH_2CH_2CHClBr$	23	146° C; gas phase;	38
	$CH_3CH_2CHBr.CH_2Cl$	22	photochemical	
	$CH_3CHBr.CH_2CH_2Cl$	55		
$CH_3CH_2CH_2CH_2F$	$CH_3CH_2CH_2CHFBr$	10		
	$CH_3CH_2CHBr.CH_2F$	9	"	"
	$CH_3CHBr.CH_2CH_2F$	81		
$CF_3CHClCH_3$	$CF_3CBrCl.CH_3$		500° C; gas phase;	127
	$CF_3CHCl.CH_2Br$	0	thermal	
$CClF_2CH_2CH_3$	$CClF_2CHBr.CH_3$	3		
	$CClF_2CH_2CH_2Br$	12	"	"
$CF_3CH_2CH_3$	$CF_3CHBr.CH_3$	9		
	$CF_3CH_2CH_2Br$	15	"	"
	$CF_3CH_2CHBr_2$	8		

Several features are noticeable in the cases of the monohalogenoalkanes:

(1) There is a marked occurence of polybromide products from the alkyl bromides which makes relative selectivities difficult to assess. These bromides probably arise from bromination of olefins formed by the elimination of Br• from the radical first formed by bromine atom attack as was discussed by Fredricks and Tedder[38] (p. 18) or by the mechanism suggested by Kharasch and co-workers[126]:

$$CH_3CH_2CH.CH_2Br + Br^{\bullet} \longrightarrow CH_3CH = CH.CH_2Br + HBr$$

(2) The true primary bonds must be attacked extremely slowly.

(3) The hydrogen atoms on the same carbon as the substituent halogen are comparatively easily attacked especially if the substituent is chlorine.

Although the high temperature employed in the bromination of the polyhalides makes comparison dangerous, it would appear that the true primary bonds are attacked more readily than the others and the rate of bromination of CF_3CH_2Br appears much slower than CF_3CH_3.

Dutch workers investigated the competitive bromination of substituted toluenes, measuring the relative rates of formation of the corresponding benzyl bromides. Their results are shown in Table 5·2. K is the reactivity of the methyl group in a substituted toluene with respect to hydrogen abstraction relative to the methyl in toluene itself.

Table 5·2. Competitive Bromination of Substituted Toluenes

Substituent	K(80° C)	Substituent	K(80° C)
pNO_2	0·11	m-Br	0·37
mNO_2	0·17	pt-butyl	1·5
pCN	0·22	p - OCH_3	6·0

Bromine showed a greater tendency to attack a point of higher electron availability than chlorine. The effect of substituents was purely polar. However this is one of the few molecules where bromination is an exothermic process. With less reactive substrates such as the alkyl mono-halides polar effects are obscured by bond strengths. Fredricks and Tedder[38] have discussed the importance of the polar effect in halogenations. They concluded that the extent to which they would be affected by polar substituents would be in the order F > Cl > Br. In the polyhalogenated alkanes, however, the polar effect of substituents appears to predominate over bond strengths despite the endothermicity of reaction for bromination.

In conclusion it would appear that the mechanism of bromination in solution is not fully understood. In the gas phase the usual radical chain mechanism normally occurs (p. 83). The formation of dibromides from hydrocarbons and the bromination of alkyl halides, especially bromides, can occur via an intermediate olefin.

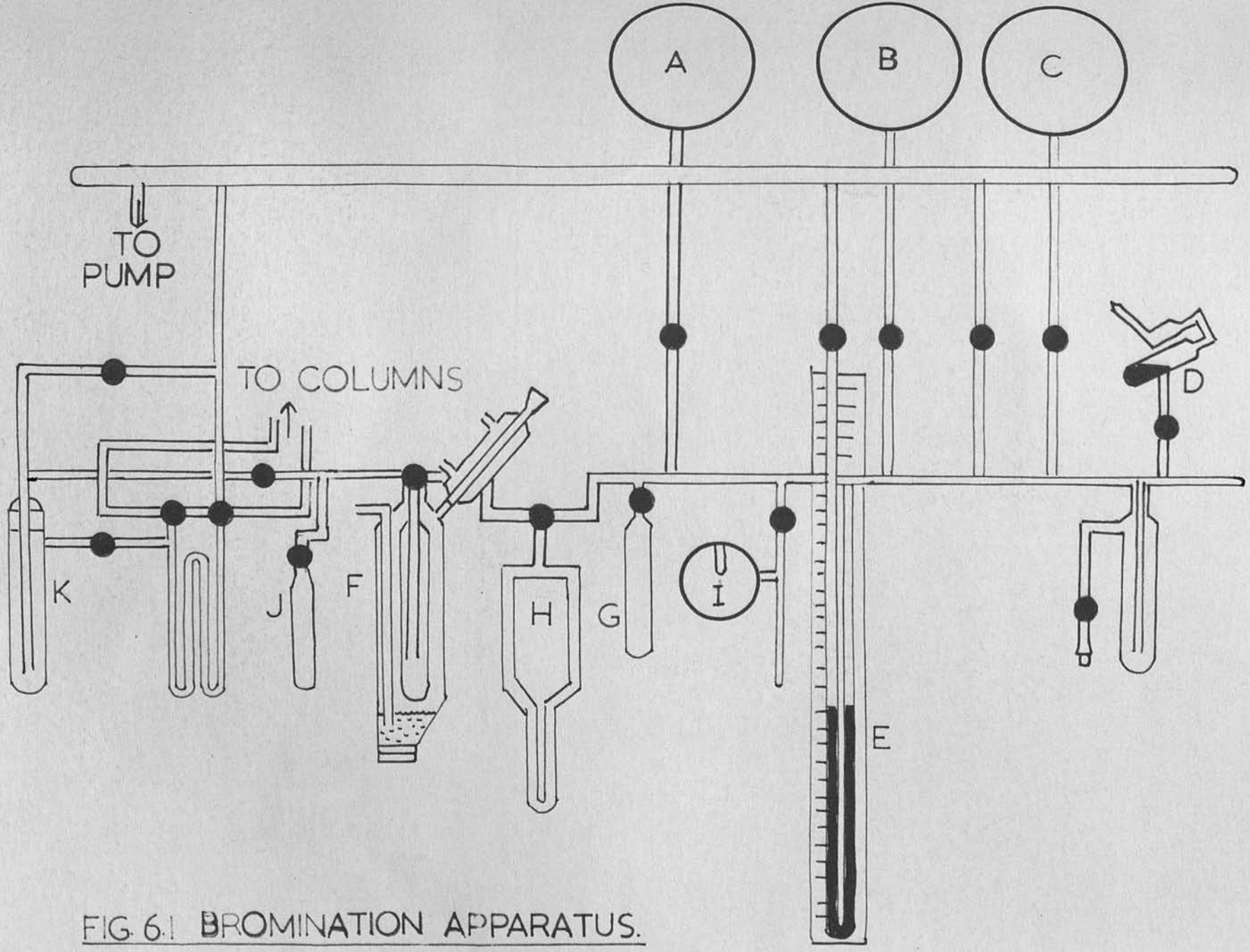


FIG. 6.1 BROMINATION APPARATUS.

CHAPTER 6.

BROMINATION EXPERIMENTAL.

It was decided that bromine hydrogen abstraction reactions should be investigated in a similar manner to fluorine. Together with the work on chlorine atoms by Knox and Nelson[2] this would give enough data to make generalisations about the halogen series.

6·1. Apparatus and Procedure.

Experiments were carried out in a static, high vacuum system built entirely of pyrex glass. All taps were greased with Edwards Silicone High Vacuum Grease. The pumping system and the pressures obtained were the same as for fluorine. The three hydrocarbon storage bulbs (Fig. 6·1) A, B, C, vacustat D and mercury manometer E were also similar to those on the fluorine apparatus. Since smaller ranges of temperature had to be used the design of the reaction vessel F was such that the temperature of the reactants could be known accurately. The reaction vessel of volume 92 cc was surrounded by a glass jacket, the bottom of which acted as a boiler which was filled with a constant boiling liquid. The liquid was boiled by passing just enough current through a spiral of resistance wire held in place round the boiler by means of alundin cement. The liquid could be drained off by pumping on a glass tube reaching to the bottom of the boiler. The reaction vessel could be held at different temperatures according to the choice of liquid. The reaction vessel was joined to the line through capillary for minimum dead space by means of a three-way tap. The outer jacket was blacked out save for a window.

The exact temperature was measured by means of a thermocouple of commercial T_1/T_2 wire in conjunction with a Doran potentiometer box. One junction was

situated in the axial well in the centre of the reaction vessel, while the other junction was held at ~20° C in a dewar of water. Calibration of the thermocouple was carried out between 20° C and 100° C using a series of thermometers accurate to 0·1° C. On extrapolation this line passed through the values of potential versus temperature supplied by the manufacturers for higher temperature. Variation in the temperature of the cold junction was allowed for using the formula:

Temperature of reaction vessel = T - (20-t)° C

Where T is the temperature corresponding to the measured potential read from the calibration graph and t is the temperature of the cold junction.

The vessel G served as a temporary storage trap. The mixing vessel H of volume 83 cc was formed in a square so that when the extended lower section was immersed in boiling water good thermal mixing occurred. The vessel was connected through a three-way tap to the line. Bulb I, of volume 500 cc, had a cold finger so that hydrocarbons could be frozen down and thermally mixed.

Bromine was stored in trap J which was attached to the line through a B14 joint. Trap K was used to degas bromine with pumping.

The chromatography W-tube and indeed the whole chromatography set-up was as for fluorine.

Procedure for a Run:-

Preparation of Hydrocarbon Mixtures:- The apparatus was pumped down to ~ 10^{-5} mm pressure before each run.

For the runs in each topic where the effects of the composition of the hydrocarbon mixture were being investigated, the small mixing vessel was used. Between 4 and 16 cm of one hydrocarbon was measured into the vessel. When the surplus hydrocarbon had been frozen back into its appropriate storage bulb and the

joining tubes thoroughly evacuated, the hydrocarbon was transferred to the small storage bulb. A suitable pressure of the second hydrocarbon was measured into the mixing vessel as above and the first hydrocarbon transferred back to join it. The frozen hydrocarbons were thoroughly degassed before being mixed.

For the bulk of the runs hydrocarbon mixtures were prepared in the 500 cc bulb, about 20 cm of a mixture being expanded into the small mixer where it was degassed and remixed ready for introduction into the reaction vessel.

Introduction of Bromine:- Immediately before each run the bromine was thoroughly degassed to remove traces of volatile material, arising probably from reaction with the tap grease. The bromine trap was surrounded by a temperature bath to give a known vapour pressure of bromine. Except where the effect of bromine pressure was being investigated an ice-water mixture was used (V.P. = 4 cm). At other times tap water (V.P. = 15 cm) and meths-water-cardice (V.P.= 34 cm) were used. Bromine at this controlled pressure was admitted into the reaction vessel, the three-way tap closed and the surplus frozen back into the storage trap.

The hydrocarbon mixture was expanded into the reaction vessel, opening the three-way tap on the mixer first to prevent back-diffusion of the bromine.

Reaction was made to take place by admitting enough light to give a suitable amount of product for analysis ($\sim 4\mu$ moles). Variation of the light was achieved with a paper shutter. Illumination from a 250 volt, 125 watt mercury vapour lamp was used for the slower reactions.

After reaction the contents of the reaction vessel were transferred to chromatography W-tube by freezing. The products were introduced into the carrier gas stream in the same way as in the fluorine work. Bromine was removed by passage through a 3" column of 3% N-N-dimethyl-p-toluidine / firebrick (52-72 mesh) before reaching the analysis columns.

6·2. Bromination Materials.

The hydrocarbons and their sources were as for fluorine unless where stated. All hydrocarbons were distilled from -80° C to -183° C over P_2O_5.

Propane (D.S.I.R. Ampoule):- was pure.

Ethane:- ehtylene was removed from B.O.G. cylinder ethane by the method of Kerr and Trotman-Dickenson[129].

Neopentane (Philips Petroleum Co. Cylinder):- contained 1% isobutane as impurity. This was removed by pre-brominating the neopentane with 5% bromine by volume for 10 min in room light. After distillation from -80° C through KOH and anhydrone, the sample still contained bromine. This was removed by passage over diethyl-p-toluidene (30%) / firebrick and a final distillation from -80° C to give a 100% pure neopentane sample.

Methane (see Topic 7):- D.S.I.R. ampoule methane and a B.O.G. cylinder sample after passage over reduced manganese dioxide were the purest.

Bromine (B.D.H.):- both analar and reagent grades were used, after standing several weeks over KBr. Small samples were distilled over KBr and P_2O_5 rejecting head and tail fractions and degassed many times by distillation from room temperature to -183° C with pumping.

Boiling Liquids:- Ether boiled under reduced pressure (16 cm) ≡ -11·5° C; ether ≡ 35° C; chloroform ≡ 58° C; ethanol ≡ 78° C water ≡ 99° C; anisole ≡ 150° C; nitrobenzene ≡ 200° C; 1-chloro-naphthalene ≡ 248° C; glycerol ≡ 284° C; mercury ≡ 340° C.

CHAPTER 7

RESULTS.

7·1. Topic No. 1. Bromination of Isobutane versus n-Butane.

The preliminary work on the development of the method was carried out in this topic. Runs were carried out on mixtures of isobutane and n-butane between -6° C and 98° C analysing for t-butyl bromide and s-butyl bromide. Other bromination products were too small to be measured.

Chromatography:- t-Butyl bromide was thought to be decomposing slightly on firebrick. For this reason celite packing was used throughout. Columns of 1½' 25% dimethyl phthalate / celite (80-100 mesh) at room temperature were used. A hydrogen flow rate of 50 cc/min eluted t-BuBr in 11 min and s-BuBr in 21 min. No other products were detected.

Pressures of Reactants:- 6·6 cm total pressure of hydrocarbon was normally used with the ratio n-butane:isobutane = 2·51:1. This ratio was varied from 3.49:1 (Run 18) to 1·51:1 (Run 20). The total pressure was varied from 8 cm (Run 24) to 4 cm (Run 25).

Normally 6 cm of bromine was used. In Run 41, 15 cm and in Run 43 3·4 cm of bromine was used. These changes in hydrocarbon and bromine pressures did not affect the results.

Conditions:-

Temp° K	261·5	284·5	308·0	331·5	371·0
Reaction Time (min)	15	6	2	4	2
Light	room	room	room	dark	dark

Effect of HBr:- In Run 44, 0·7 cm hydrogen was illuminated with the lamp for 15 min with 6 cm bromine. 6·6 cm hydrocarbon were then added and a normal run executed. No change in the result was found.

No bromination was found to occur after the products were taken from the reaction vessel. This was proved by placing the normal mixture of bromine and hydrocarbon in the chromatography W-tube, giving it the same treatment of freezing and heating up as for a run. Analysis revealed negligible amounts of bromides.

The bromine absorption tube was proved to have no effect on the products by:

(1) Varying its length. The result was not affected.

(2) Passing known mixtures of bromides through the columns. Only slight variation from the measured injected ratio could be detected. The column proved to be a very efficient bromine remover. The material turned brown on complete bromination and could be easily renewed.

Where $k_{ti\text{-}Bu}$ and $k_{sn\text{-}Bu}$ are the rate constants of

$$Br\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3C\cdot + HBr$$

and $$Br\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3\dot{C}HCH_2CH_3 + HBr$$

respectively, then

$$\frac{k_{ti\text{-}Bu}}{k_{sn\text{-}Bu}} = \frac{(t\text{-BuBr})}{(s\text{-BuBr})} \times \frac{(n\text{-Bu})}{(i\text{-Bu})}$$

Sample Run

Run 20 Temperature = 284·5° K

Reactant	Pressure in Reaction Vessel (cm)
n-butane	4·10
isobutane	2·72
bromine	6·0

Peak area t-BuBr = 10·30 units

" " s-BuBr = 0·95 units

$$\frac{k_{ti\text{-}Bu}}{k_{sn\text{-}Bu}} = \frac{10.30}{0.95} \times \frac{4.10}{2.72} = 16.35$$

The results are given in Table 7·1 and the Arrhenius plot in Fig. 7·1. A least squares' treatment of these results gives the equation of the line uncorrected for gauge sensitivities:

$$\frac{k_{ti\text{-}Bu}}{k_{sn\text{-}Bu}} = 0.132 \pm 0.009 \exp (2716 \pm 30/RT).$$

Table 7·1. Results of Isobutane / n-Butane Bromination.

Run No.	Temp° K	Hydrocarbon Press. (cm) n-Butane	Isobutane	Peak Areas (Units) t-BuBr	s-BuBr	$k_{ti\text{-}Bu}/k_{sn\text{-}Bu}$
56	261·5	4·73	1·88	9·48	1·00	23·93
57	"	"	"	12·30	1·12	27·60
58	"	"	"	8·36	0·82	25·84
61	"	"	"	8·59	0·86	25·12
54	267·0	"	"	11·73	1·29	22·89
55	"	"	"	10·33	1·28	20·30
18	284·5	5·29	1·51	6·20	1·40	15·58
20	"	4·10	2·72	10·30	0·95	16·35
24	"	5·80	2·31	5·36	0·86	15·65
25	"	3·00	1·20	5·34	0·77	16·94
26	"	4·73	1·88	9·03	1·38	16·46
27	"	"	"	5·57	0·88	15·92
28	"	"	"	11·25	1·67	16·95
29	"	"	"	6·04	0·96	15·83
39	308·0	5·19	2·07	7·68	1·81	10·63
40[a]	"	3·82	1·52	3·05	0·69	11·09
41[a]	"	3·26	1·30	2·11	0·49	10·80
43[b]	"	4·73	1·88	3·03	0·68	11·16
44[c]	"	3·51	1·40	16·04	3·61	11·14
45	331·5	4·73	1·88	6·04	1·73	8·78
46	"	"	"	3·10	0·98	7·94
48	"	"	"	2·77	0·79	8·83
50	"	"	"	5·21	1·65	7·94
51	"	"	"	9·08	3·02	7·56

Table 7·1 (continued)

Run No.	Temp° K	Hydrocarbon Press. (cm) n-Butane	Isobutane	Peak Areas (Units) t-BuBr	s-BuBr	$k_{ti\text{-}Bu}/k_{sn\text{-}Bu}$
30	371·0	4·73	1·88	5·08	2·29	5·58
33	"	"	"	1·86	0·93	5·03
34	"	"	"	3·17	1·46	5·45
35	"	"	"	1·60	0·77	5·23
36	"	"	"	1·29	0·61	5·32
37	"	"	"	2·52	1·13	5·61

a. Bromine pressure = 15 cm b. Bromine pressure = 3·4 cm

Bromine pressure for all other runs = 6 cm

c. 3 mm HBr also present.

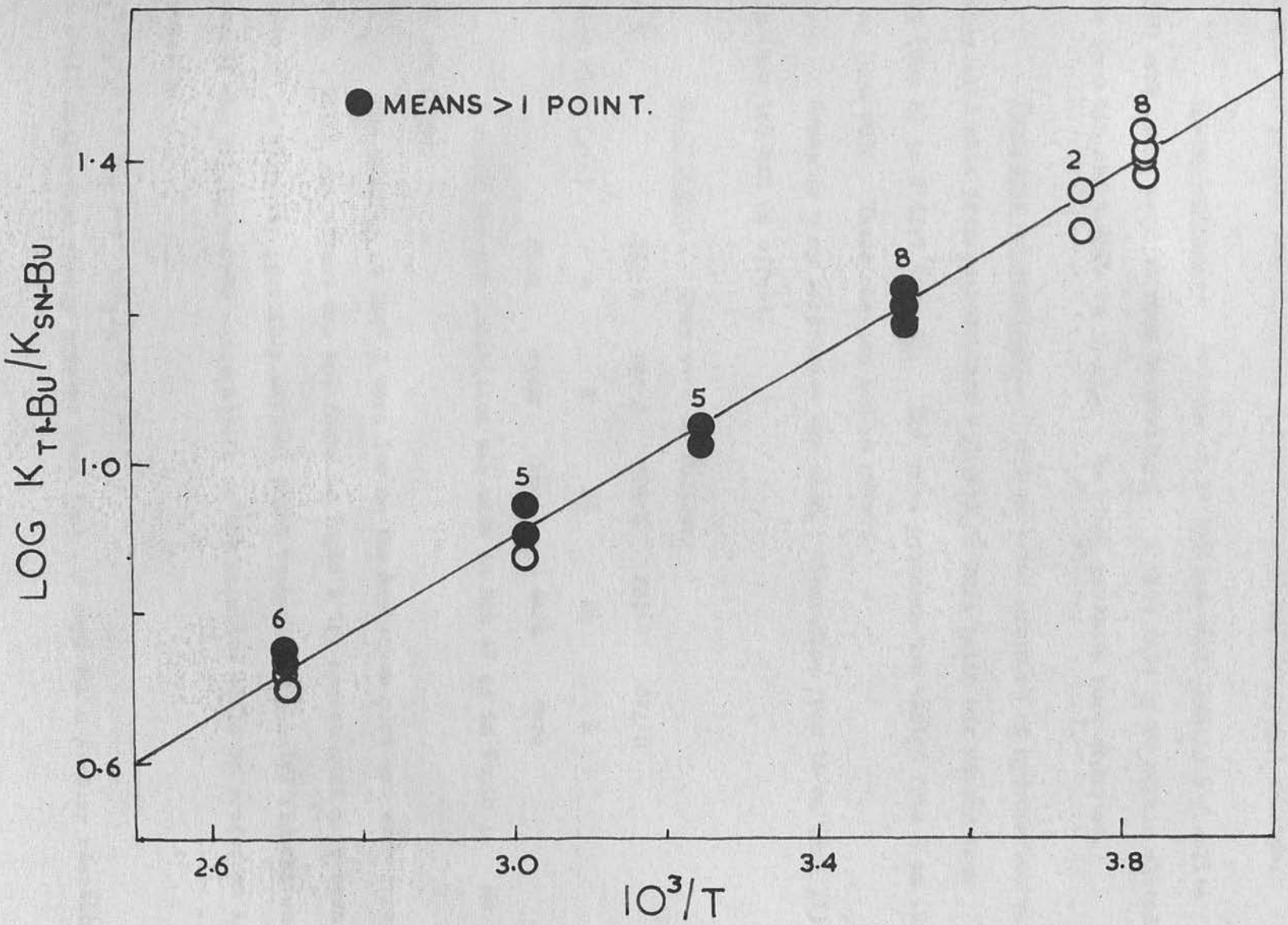

MEANS > 1 POINT.
LOG $K_{T\text{-}Bu}/K_{SN\text{-}Bu}$
1·4
1·0
0·6
2·6
3·0
3·4
3·8
$10^3/T$
6
5
5
8
2
8

FIG. 7.1.

7·2. Topic No. 2. Bromination of Isobutane versus Propane.

Runs were carried out between 34° C and 148° C on mixtures of isobutane and propane analysing for t-butyl bromide and isopropyl bromide.

Chromatography:- Columns of 2' 25% dimethyl phthalate / celite (80-100 mesh) were used at room temperature. A flow rate of 50 cc/min eluted s-PrBr in 9 min and t-BuBr in 15 min. No other products were detected.

Pressures of Reactants:- 6·6 cm total pressure of hydrocarbon was normally used with propane:isobutane = 3·45:1. This ratio was varied from 2·12:1 (Run 8) to 4·41:1 (Run 9). The total pressure was varied from 8 cm (Run 13) to 4 cm (Run 10). These changes had no effect.

Normally 6 cm of bromine was used. Variation from 15 cm (Run 17) to 3·4 cm (Run 18) had no effect.

Conditions:- They were as follows:

Temp° K	261·5	284·5	308·0	331·5	371·0
Reaction Time (min)	8	6	$3\frac{1}{2}$	$2\frac{1}{2}$	1
Light	room	room	room	dark	dark

A check for HBr inhibition was made in Run 47 as in Topic 1. No effect was found.

The results at 284° K were low on the Arrhenius plot and were irreproducible. Since the effect was not found in Topic 3 the reason must have been the presence of an impurity (probably oxygen) which removed the t-butyl radical and so lowered the t-BuBr/s-PrBr ratio; attack on the impurity would be preferred if the reaction,

$$(CH_3)_3C\cdot + Br_2 \longrightarrow (CH_3)_3CBr + Br\cdot$$

had a small activation energy greater than that (if any) for a similar reaction with

impurity. For this to be valid the isopropyl radical should have virtually zero activation energy for its analogous reaction with bromine.

At higher temperatures another effect occurred. As the vacuum fell throughout the day, (due perhaps to bromine attack on the diffusion-pump mercury) the amount of reaction fell correspondingly. The ratio was not affected until the amount of reaction fell below 50% of the result under the best vacuum conditions. The inhibitor may have been oxygen, since the addition of small amounts of air to the reaction system inhibited the reaction completely. Its effect seemed to increase as the temperature fell. For this reason the results at 284° K were neglected.

Impurity effects were not so apparent as in Topic 1, presumably because the mercury was clean and the glass grease-free and little degassing occurred.

Where $k_{ti\text{-}Bu}$ and k_{sPr} are the rate constants of

$$Br\cdot + (CH_3)_3CH \longrightarrow HBr + (CH_3)_3C\cdot$$

and $$Br\cdot + CH_3CH_2CH_3 \longrightarrow HBr + CH_3\dot{C}HCH_3$$

respectively, then

$$\frac{k_{ti\text{-}Bu}}{k_{sPr}} = \frac{(t\text{-}BuBr)}{(s\text{-}PrBr)} \times \frac{(Pr)}{(i\text{-}Bu)}.$$

The results are given in Table 7·2 and the Arrhenius plot in Fig. 7·2. A least squares' treatment of these results gives the equation of the line uncorrected for gauge sensitivities:

$$\frac{k_{ti\text{-}Bu}}{k_{sPr}} = 0{\cdot}418 \pm 0{\cdot}040 \exp (2640 \pm 65/RT).$$

Table 7·2. Results of Isobutane / Propane Bromination.

Run No.	Temp T °K	$\frac{k_{ti\text{-}Bu}}{k_{sPr}}$	Run No.	Temp T °K	$\frac{k_{ti\text{-}Bu}}{k_{sPr}}$
2	307·5	33·92	51	371·5	15·99
4	"	34·67	16	"	13·30
5	"	28·18	17	"	13·20
6	"	29·80	18	"	13·42
7	"	29·65	19	"	14·60
8	331·5	23·10	38	421·0	8·92
9	"	25·40	41	"	9·26
10	"	24·90	42	"	10·01
11	"	23·40	43	"	11·40
13	"	21·80	44	"	9·07
39	"	23·35	45	"	10·02
48	371·5	16·60	46	"	10·20
49	"	14·97	47	"	10·31
50	"	15·25			

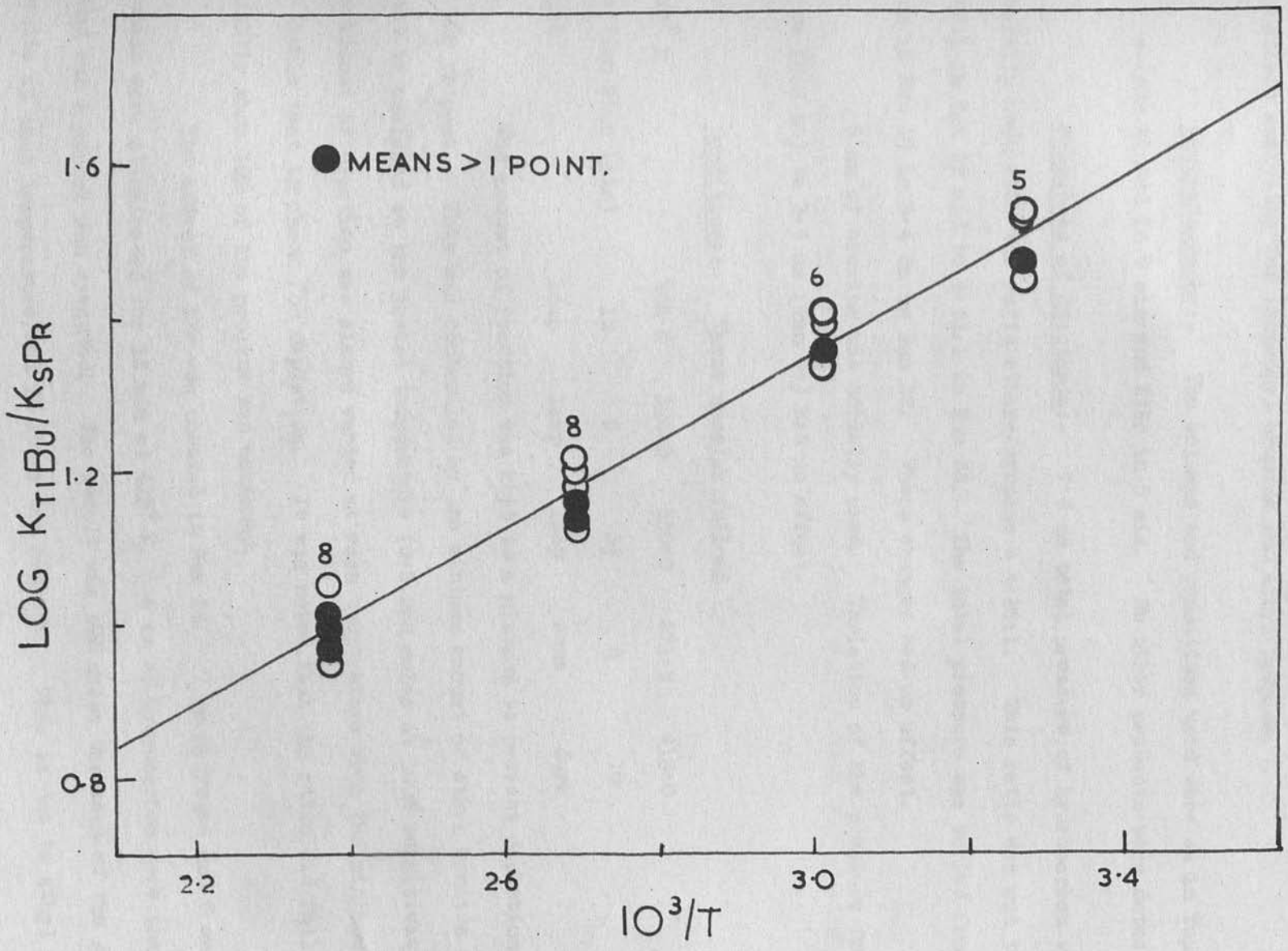


FIG. 7.2.

7·3. Topic No 3. Bromination of Propane versus Ethane.

Runs were carried out between 12·5° C and 145° C on mixtures of propane and ethane analysing for isopropyl bromide and ethyl bromide.

Chromatography:- The columns and conditions used were as in Topic 2. s-PrBr eluted in 9 min and EtBr in 5 min. No other products were detected.

Pressures of Reactants:- 7·6 cm total pressure of hydrocarbon was generally used with the ratio ethane/propane = 4·88:1. This ratio was cut to 2·03:1 in Run 32 and to 1·43:1 in Run 33. The total pressure was varied from 5 cm in Run 35 to 8·4 cm in Run 36. These changes had no effect.

6 cm of bromine was normally used. Variation of the pressure from 15 cm (Run 25) to 3·4 cm (Run 26) had no effect.

Conditions:- These were as follows

Temp° K	285·5	306·0	330·0	371·5	418·0
Reaction Time (min)	12	5	3½	6	10
Light	lamp	lamp	lamp	room	dark

The amount of reaction was kept to a minimum to prevent depletion of the propane. This was controlled by the minimum amount of ethyl bromide which could be analysed at the lowest temperature (0·3-05μ moles at 100% sensitivity). The amount of reaction was always varied at each temperature from the minimum possible to treble that to check for depletion. It was noted that the ratio did fall slightly when 10% of the propane was consumed.

The effect of HBr was checked in Run 38. 1 cm hydrogen and 6 cm bromine were illuminated for 15 min at 418° K. 6 cm of hydrocarbon were than added and a normal run executed. The result was 10% above the mean of the general results at that temperature, and 2% above the highest. This is due to ethyl radicals

reacting with HBr, of which too much had been produced in relation to the amount formed during a normal run (20 times the mean (HBr)). However since the effect is not large even with this excess of HBr, the results for a normal run will be accurate.

Where k_{sPr} and k_{Et} are the rate constants of

$$Br\cdot + CH_3CH_2CH_3 \longrightarrow HBr + CH_3\dot{C}HCH_3$$

and $$Br\cdot + CH_3CH_3 \longrightarrow HBr + CH_3\dot{C}H_2$$

respectively, then

$$\frac{k_{sPr}}{k_{Et}} = \frac{(s\text{-PrBr})}{(EtBr)} \times \frac{(Et)}{(Pr)}.$$

The results are given in Table 7·3 and the Arrhenius plot in Fig. 7·3. A least squares' treatment of all the results gives the equation of the line uncorrected for gauge sensitivities:

$$\frac{k_{sPr}}{k_{Et}} = 0{\cdot}669 \pm 0{\cdot}053 \exp (3247 \pm 51/RT).$$

Table 7·3. Results of Propane / Ethane Bromination.

Run No.	Temp T °K	$\frac{k_{sPr}}{k_{Et}}$	Run No.	Temp T °K	$\frac{k_{sPr}}{k_{Et}}$
17	285·5	237·4	30	330·0	96·65
18	"	225·4	1	371·3	52·81
20	"	201·4	2	"	51·14
21	"	190·0	3	"	46·95
22	"	232·0	4	"	57·90
23	"	193·1	5	"	50·51
9	306·0	129·9	6	"	53·93
10	"	135·8	7	"	50·79
12	"	131·3	31	418·0	28·87
13	"	135·5	32	"	33·57
14	"	138·0	33	"	33·81
24	330·0	86·80	34	"	35·32
25	"	99·40	35	"	37·84
26	"	102·3	36	"	35·94
27	"	86·10	37	"	37·56
28	"	107·4	38	"	39·54
29	"	104·3			

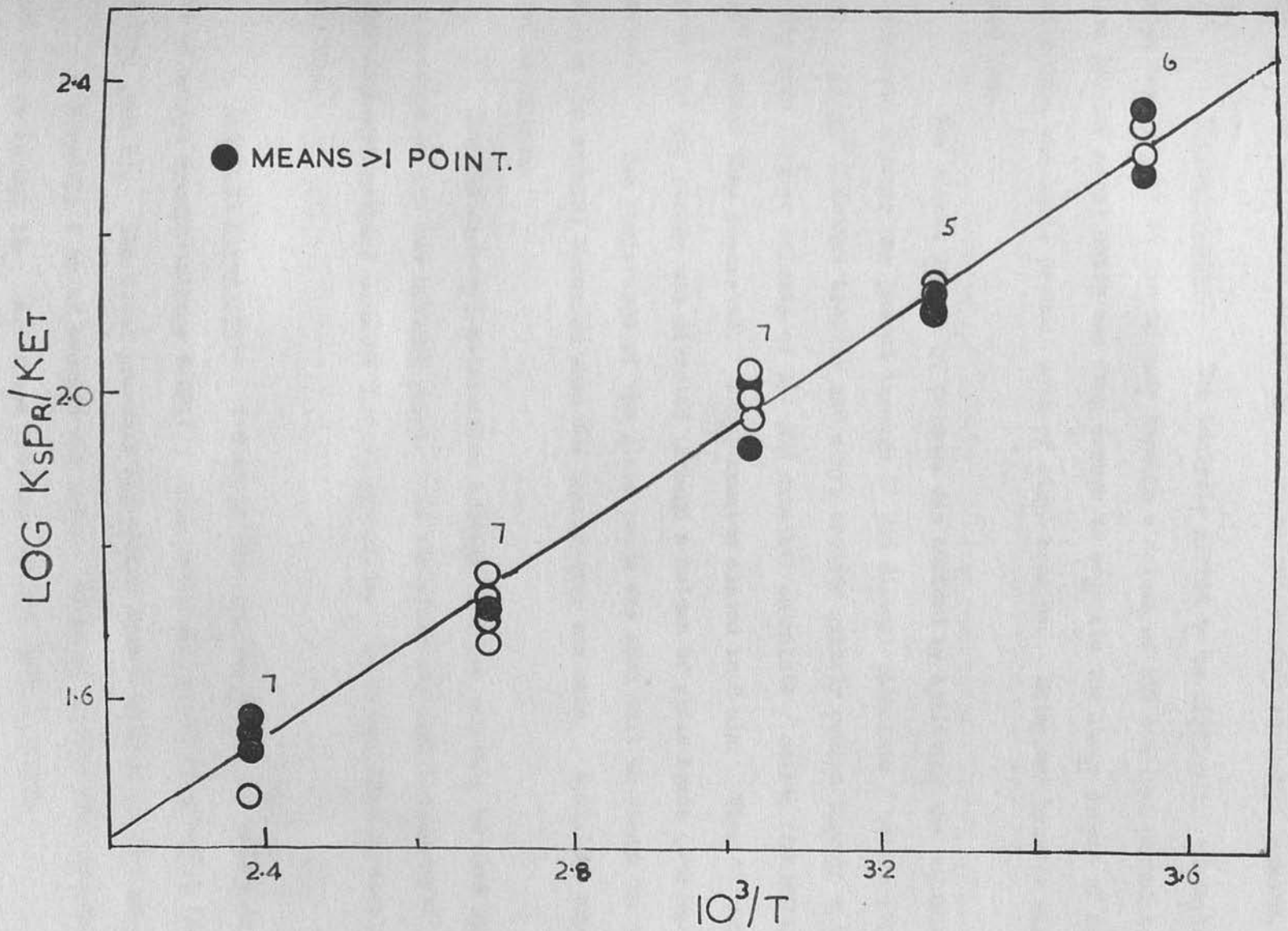


FIG. 7.3.

7·4. Topic No. 4 Bromination of Methyl Bromide versus Ethane.

Runs were carried out between 58·5° C and 199° C on mixtures of methyl bromide and ethane analysing for methylene bromide and ethyl bromide.

Chromatography:- The analysis proved to be difficult. Methylene bromide took almost 60 min to come through a column of 25% dimethyl phthalate / celite (80-100 mesh) which was long enough to separate the large excess of methyl bromide from the small product peak of ethyl bromide. Methylene bromide was not a good peak.

The excess length of columns was avoided by splitting the columns. The analysis mixture was passed through 5' 25% dinonyl phthalate / celite (72-100 mesh). At 70° C methyl bromide and ethyl bromide quickly passed through a two-way tap onto further columns of 1½' 25% dimethyl phthalate / celite (80-100 mesh) at 25° C, where they separated. Ethyl bromide eluted in 6 min. When it had been recorded the gas stream was diverted through a column of glass beads (0·2 mm diameter). The resistance of the glass beads was such that no change in the flow rate (90 cc/min) occurred when the change-over was made. Methylene bromide eluted in 15 min.

The N-N-dimethyl-p-toluidine bromine absorber can only be used up to 50° C because of its low boiling point. In its place was used tetramethyl-diamino-diphenyl-methane plus 3% dinonyl phthalate. It turned blue on complete exhaustion.

Reactant Pressures:- 7·6 cm of reactant was generally used with the ratio of methyl bromide:ethane 4·29:1. This ratio was varied from 3·10:1 (Run 4) to 2·11:1 (Run 5). The total pressure was varied from 6 cm (Run 2) to 9 cm (Run 3).

Normally 6 cm of bromine was used. 15 cm of bromine was used in Run 10 and 3·4 cm in Run 11. All these pressure changes had no effect.

Conditions:- These were as follows:

Temp° K	331·5	371·5	420·0	472·0
Reaction Time (min)	25	14	10	3
Light	lamp	lamp	lamp	lamp

The effect of HBr on the reaction of bromine with methyl bromide has been investigated[84]. No inhibition was found. Ethane has been investigated in Topic 3.

Although the ratios of rate constants are reproducible the results at 331° K are high on the Arrhenius plot. This is probably due to loss of methylene bromide in tap grease which would be most important at the low temperature where small amounts of methylene bromide had to be measured. For this reason the activation energy recorded may be slightly high.

Where k_{Et} and k_{MeBr} are the rate constants of

$$CH_3CH_3 + Br\cdot \longrightarrow CH_3CH_2\cdot + HBr$$

and $$CH_3Br + Br\cdot \longrightarrow CH_2Br\cdot + HBr$$

respectively, then

$$\frac{k_{Et}}{k_{MeBr}} = \frac{(EtBr)}{(CH_2Br_2)} \times \frac{(MeBr)}{(Et)}.$$

The results are given in Table 7·4 and the Arrhenius plot in Fig. 7·4. A least squares' treatment of these results gives the equation of the line uncorrected for gauge sensitivities:

$$\frac{k_{Et}}{k_{MeBr}} = 1{\cdot}327 \pm 0{\cdot}122 \exp (2654 \pm 88/RT).$$

Table 7·4. Results of Ethane / Methyl Bromide Bromination.

Run No.	Temp T °K	$\frac{k_{Et}}{k_{MeBr}}$	Run No.	Temp T °K	$\frac{k_{Et}}{k_{MeBr}}$
13	331·5	74·40	2	420·0	29·53
14	"	80·98	3	"	34·98
15	"	76·42	4	"	31·32
16	"	79·73	5	"	31·69
17	"	76·42	6	"	29·51
18	"	81·51	19	472·0	21·65
7	371·5	45·65	20	"	23·60
8	"	46·48	21	"	23·00
9	"	42·91	22	"	23·44
10	"	44·27	23	"	22·74
11	"	44·43	24	"	22·10
1	420·0	36·83			

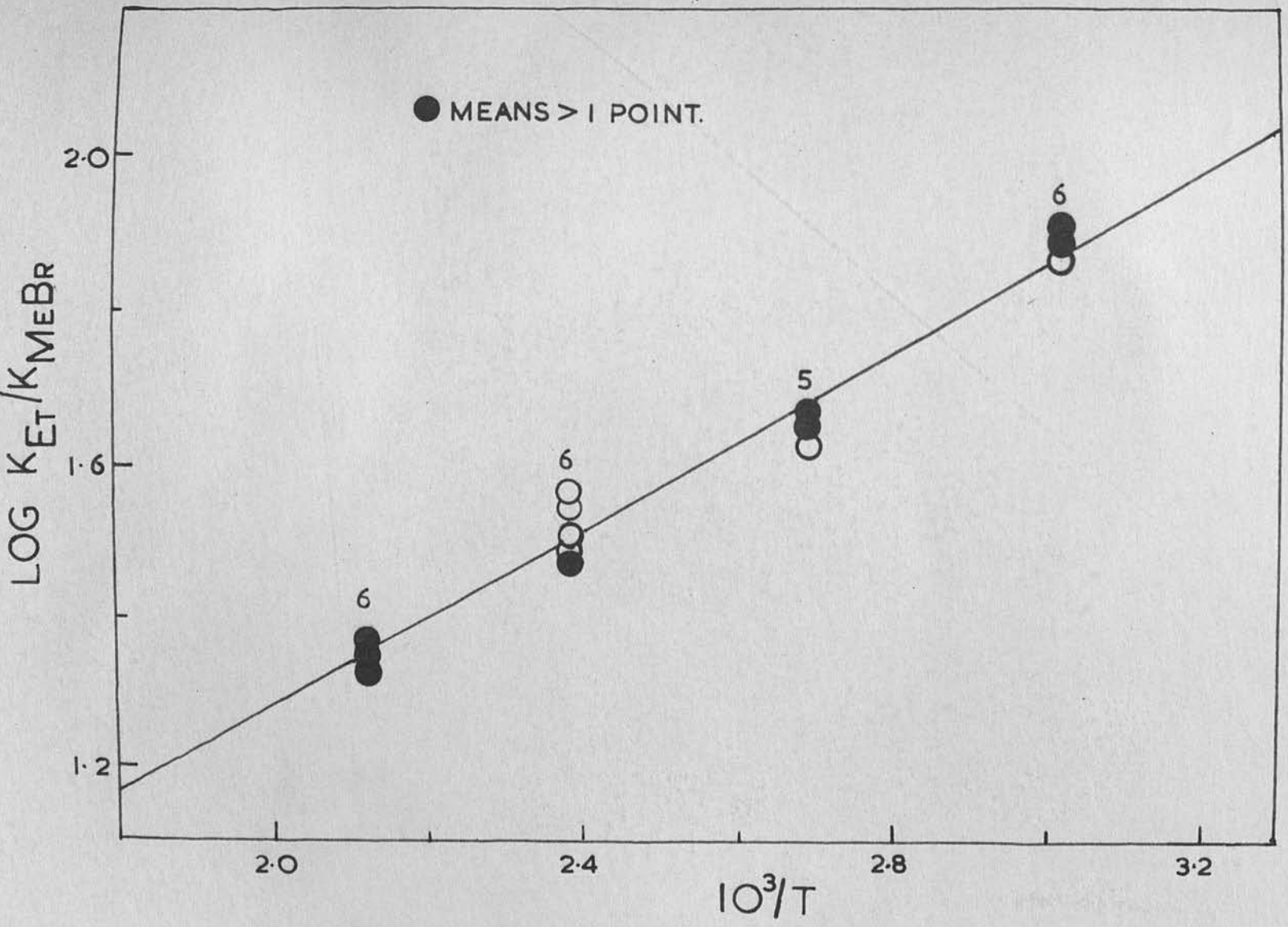


FIG. 7.4.

7·5. Topic No. 5. Bromination of Neopentane versus Ethane.

Runs were carried out between 57° C and 200° C on mixtures of neopentane and ethane analysing for neopentyl bromide and ethyl bromide.

Chromatography:- The columns used were 2' 25% dimethyl phthalate / celite (80-100 mesh) held at room temperature. A flow rate of 96 cc/min eluted EtBr in 3 min and neo-PBr in 16 min. No other products were detected.

Reactant Pressures:- 6·6 cm of hydrocarbon was generally used with the ratio neopentane:ethane = 1·00:1. This ratio was varied from 1:1·52 (Run 1) to 1·51:1 (Run 2). The total hydrocarbon pressure was varied from 8 cm (Run 5) to 4 cm (Run 6).

6 cm of bromine was normally used. This pressure was varied from 15 cm (Run 15) to 3·4 cm (Run 16). All these pressure changes had no effect.

Conditions:- These were as follows:

Temp° K	330·0	371·5	420·5	473·0
Reaction Time (min)	12	6	$2\frac{1}{2}$ + 3	6
Light	lamp	lamp	lamp	room room

Where k_{neoP} and k_{Et} are the rate constants of

$$(CH_3)_4C + Br\cdot \longrightarrow (CH_3)_3C.CH_2\cdot + HBr$$

and $$CH_3CH_3 + Br\cdot \longrightarrow CH_3CH_2\cdot + HBr$$

respectively, then

$$\frac{k_{neoP}}{k_{Et}} = \frac{(\text{neo-PBr})}{(\text{EtBr})} \times \frac{(\text{Et})}{(\text{neo-P})}.$$

The results are given in Table 7·5 and the Arrhenius plot in Fig. 7·5. A least squares' treatment of these results gives the equation of the line uncorrected for gauge sensitivities.

$$\frac{k_{neo\text{-}P}}{k_{Et}} = 2{\cdot}483 \pm 0{\cdot}117 \exp(-893 \pm 44/RT).$$

Table 7·5. Results of Neopentane / Ethane Bromination

Run No.	Temp T °K	$\frac{k_{neoP}}{k_{Et}}$	Run No.	Temp T °K	$\frac{k_{neoP}}{k_{Et}}$
8	330·0	0·65	1	420·5	0·86
9	"	0·66	2	"	0·90
10	"	0·63	3	"	0·80
11	"	0·63	4	"	0·79
12	"	0·62	5	"	0·83
14	371·5	0·82	6	"	0·79
15	"	0·71	22	473·0	0·98
16	"	0·72	23	"	0·92
18	"	0·79	24	"	1·05
19	"	0·72	25	"	1·02
20	"	0·71	26	"	0·93
21	"	0·77			

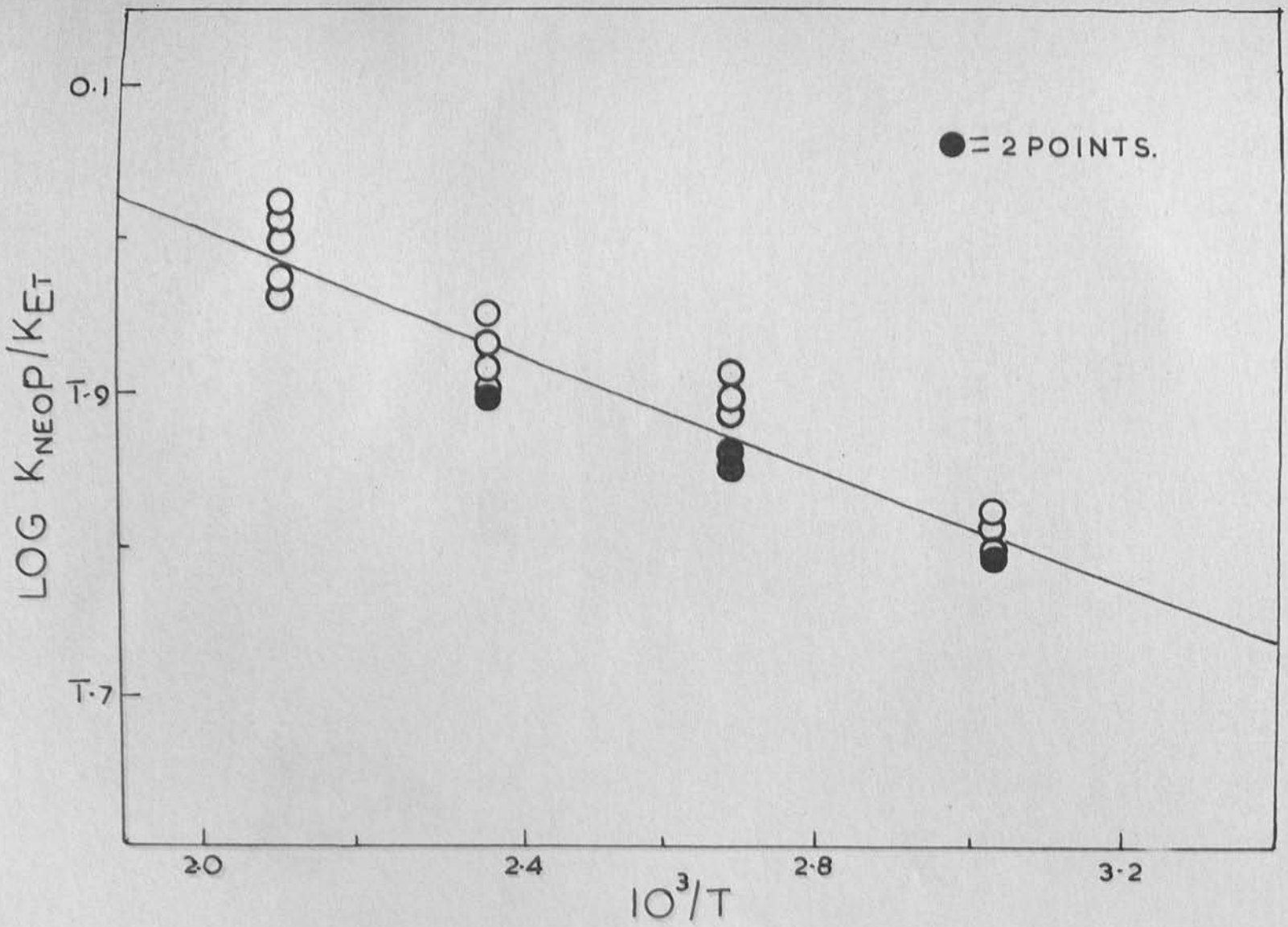


FIG. 7.5.

7·6. Topic No. 6. Bromination of Methyl Chloride versus Ethane.

Runs were carried out between 58·5° C and 200° C on mixtures of methyl chloride and ethane analysing for bromo-chloro-methane and ethyl bromide.

Chromatography:- The columns used were 2' 25% dimethyl phthalate / celite (80-100 mesh) held at room temperature. A flow rate of 64 cc/min eluted EtBr in 3 min and CH_2ClBr in 15 min. No other products were detected.

Reactant Pressures:- 6·6 cm total pressure of hydrocarbon were generally used with the ratio of methyl chloride:ethane = 2·91:1. This ratio was reduced from 1·92:1 (Run 1) to 1·01:1 (Run 3). The total hydrocarbon pressure was varied from 4 cm (Run 2) to 8 cm (Run 4).

The bromine pressure normally used was 6 cm. This pressure was varied from 3·4 cm (Run 16) to 15 cm (Run 17). All these pressure changes had no effect.

Conditions:- These were as follows:

Temp° K	331·5	371·5	409·0	473·0
Reaction Time (min)	20	15	10	3
Light	lamp	lamp	lamp	lamp

The effect of HBr was investigated in Run 35 when 6 cm of hydrogen was illuminated with 12 cm bromine for 40 min, the products frozen down and the unreacted hydrogen pumped away. The products and bromine were heated up and half of them returned to the reaction vessel. This gave an amount of HBr equivalent to that formed during a normal run. The result was not affected.

The results were not as reproducible as in previous topics. This appeared to be associated with the methyl chloride. The intermediate radical was probably sensitive to impurity.

Where k_{Et} and k_{MeCl} are the rate constants of

$$CH_3CH_3 + Br\cdot \longrightarrow CH_3CH_2\cdot + HBr$$

and

$$CH_3Cl + Br\cdot \longrightarrow ClCH_2\cdot + HBr$$

respectively, then

$$\frac{k_{Et}}{k_{MeCl}} = \frac{(EtBr)}{(CH_2ClBr)} \times \frac{(MeCl)}{(Et)}.$$

The results are given in Table 7·6 and the Arrhenius plot in Fig. 7·6. A least squares' treatment of these results gives the equation of the line uncorrected for gauge sensitivities.

$$\frac{k_{Et}}{k_{MeCl}} = 1{\cdot}936 \pm 0{\cdot}109 \exp (1055 \pm 68/RT).$$

Table 7·6. Results of Ethane / Methyl Chloride Bromination

Run No.	Temp T °K	$\frac{k_{Et}}{k_{MeCl}}$	Run No.	Temp T °K	$\frac{k_{Et}}{k_{MeCl}}$
30	331·5	10·70	21	371·5	8·23
31	"	9·66	22	"	8·69
32	"	9·39	23	"	8·24
33	"	9·66	26	409·0	6·59
34	"	8·89	27	"	7·63
35	"	10·48	28	"	7·04
8	371·5	7·94	29	"	7·52
10	"	7·10	1	473·0	5·85
11	"	7·20	2	"	5·78
14	"	8·97	3	"	6·27
16	"	7·78	4	"	5·22
17	"	8·32	5	"	5·75
20	"	7·40	7	"	7·30

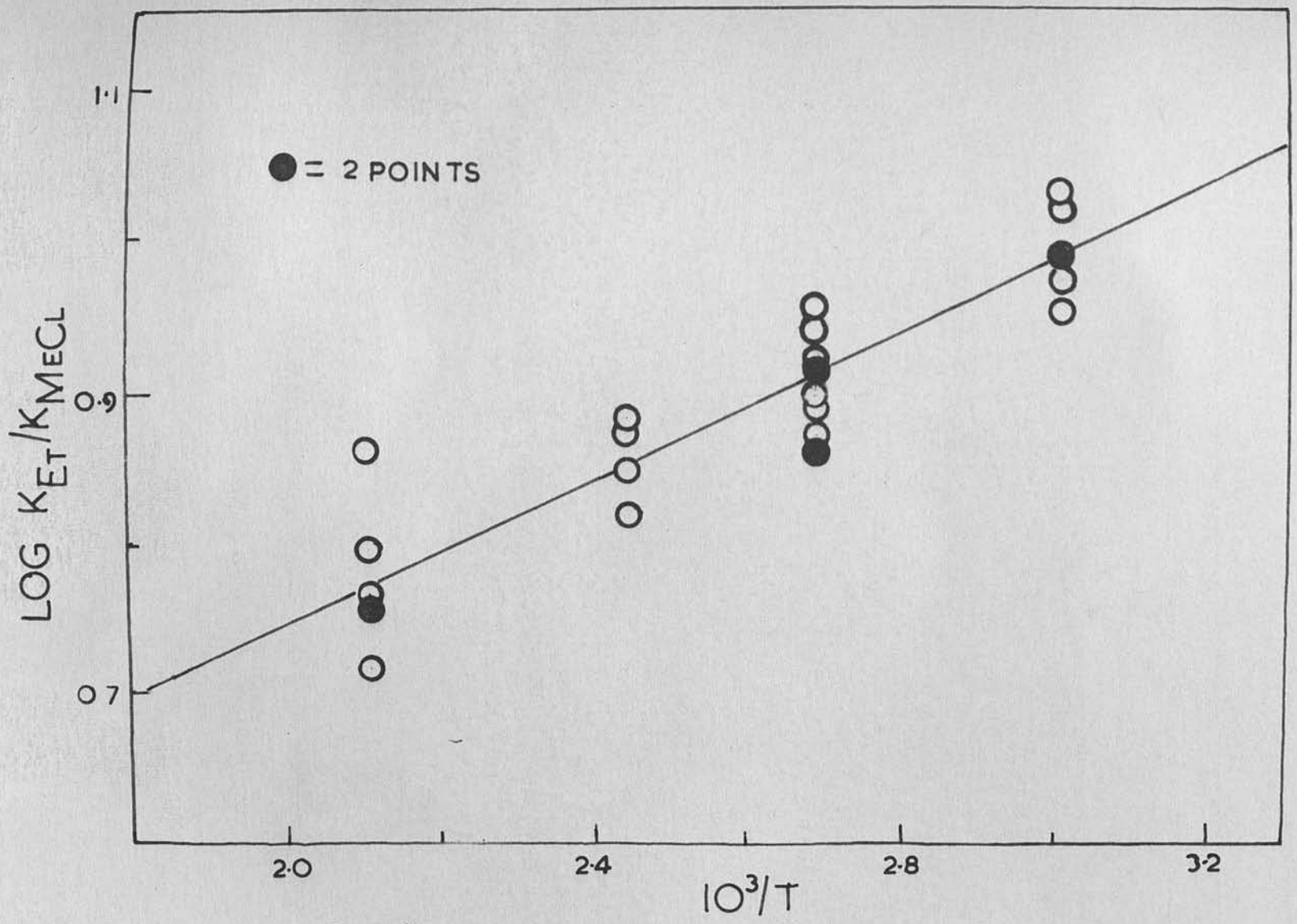


FIG. 7.6.

7·7. Topic No. 7. Bromination of Methane versus Methyl Chloride.

Runs were carried out between 204° C and 341° C on mixtures of methane and methyl chloride analysing for methyl bromide and chloro-bromo-methane.

The topic proved to be very difficult. The results with cylinder methane which had been passed over copper oxide reduced at 350° C in a stream of hydrogen and subsequently degassed at -210° C, were irreproducible and unreasonable. As the temperature of reaction was lowered the amount of CH_2ClBr produced fell unreasonably. At 423° K no CH_2ClBr was produced. When methyl chloride was brominated alone this effect was not observed. An impurity in the methane must have been the cause.

Addition of ethane equivalent to the methyl chloride pressure to the system raised the CH_2ClBr/MeBr ratio. However the same result was obtained at 473° K and 557° K.

A sample of D.S.I.R. pure methane gave good consistent results at 473° K and 557° K provided ethane was present. The ethyl radical, being present in large excess removed the impurity which destroyed the $CH_2Cl\cdot$ radical (at all temperatures in the absence of ethane the amount of CH_2ClBr was inconsistently low). At 614° K the results were again low. This was probably due to the depletion of bromine by the fast reacting ethane. At this point the supply of D.S.I.R. methane ran out.

Attempts were made to remove the impurity from cylinder methane by pre-bromination in the presence of ethane. This was partially successful. Passage of the methane over manganese dioxide reduced at 300° C in a stream of hydrogen and several trap (-183° c) to trap (-210° C) distillations with pumping produced a methane which gave consistent results at 614° K and 521° K in the presence of ethane. The result at 423° K was the highest obtained with or without

ethane present but was still unreasonably low (k_{MeCl}/k_{Me} = 17·04).

Chromatography:- The columns used were 5' 25% diethyl phthalate / celite (80-100 mesh) held at 37° C. A flow rate of 60 cc/min eluted MeBr in 3 min and CH_2ClBr in 26 min.

Reactant Pressures:- The total pressure of hydrocarbon generally used was 7·41 cm with $CH_3Cl:CH_4:C_2H_6$ = 1·7:5:0:7. The total pressure was varied from 5·11cm (Run 14) to 10·12cm (Run 13). The ratio of $CH_3Cl:CH_4$ was varied from 1:2·99 (Run 12) to 1·39:1 (Run 16). No great effect was observed.

The ethane pressure was varied from 0·3 cm (Run 7) to 2 cm (Run 10) Outwith this pressure range the results came low.

The bromine pressure was maintained as high as possible (~10 cm). Lowering of the pressure gave low results (impurity attacked $\cdot CH_2Cl$ in place of bromine).

Conditions:- These were as follows

Temp° K	477	521	557	614
Reaction Time (min)	15	8	5	5
Light	lamp	lamp	lamp	room.

Since variation of the ethane pressure over the range indicated did not affect the result, hydrogen bromide which was a product of the fast reacting ethane did not affect the result in the concentrations formed during a normal run.

Where k_{Me} and k_{MeCl} are the rate constants of

$$CH_4 + Br\cdot \longrightarrow CH_3\cdot + HBr$$

and $$CH_3Cl + Br\cdot \longrightarrow ClCH_2\cdot + HBr$$

respectively, then

$$\frac{k_{MeCl}}{k_{Me}} = \frac{(CH_2ClBr)}{(MeBr)} \times \frac{(Me)}{(MeCl)}.$$

The results are given in Table 7·7. The results were not accurate enough to merit a least squares' treatment. The best line through the mean points in the Arrhenius plot (Fig. 7·7.) was taken.

$$\frac{k_{MeCl}}{k_{Me}} = 0{\cdot}360 \exp (3799/RT).$$

Table 7·7. Results of Methyl Chloride / Methane Bromination

Run No.	Temp T °K	$\frac{k_{MeCl}}{k_{Me}}$	Run No.	Temp T °K	$\frac{k_{MeCl}}{k_{Me}}$
5	477	24·17	12	557	11·93
6	"	23·32	13	"	11·22
7	"	17·42	14	"	13·85
8	"	20·32	15	"	12·15
9	"	21·11	16	"	14·35
10	"	17·46	Mean Result	"	12·70
11	"	25·47	25	614	7·47
Mean Result	"	21·32	26	"	5·17
20	521	11·14	27	"	6·67
21	"	14·14	28	"	8·60
22	"	13·20	29	"	6·97
23	"	11·61	30	"	7·50
24	"	12·02	Mean Result	"	7·06
Mean Result	"	12·42			

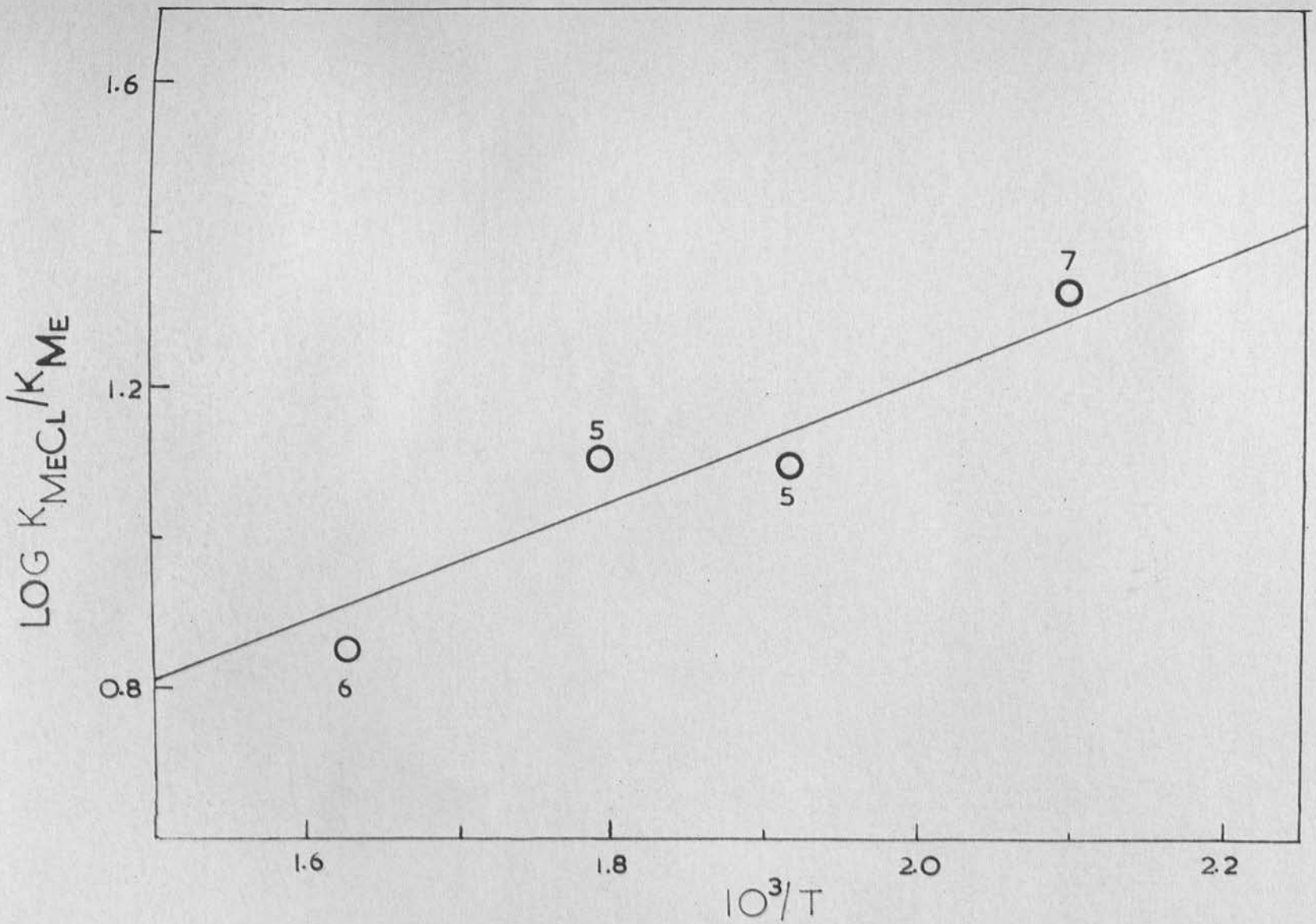


FIG. 7.7. PLOT OF MEAN POINTS.

7·8. Calibration of Bromide Peak Areas.

Calibrations were carried out on mixtures of pairs of bromides. A known mixture was injected into the chromatography columns and the relative peak areas of the eluted bromides measured.

Chromatography:- With the exception of methylene bromide / ethyl bromide and chloro-bromo-methane / methyl bromide mixtures all the bromides were measured on a column 2' 25% dimethyl phthalate / celite (80-100 mesh) with a flow rate of 96 cc/min. The columns in Topics 4 and 7 were used for the exceptions respectively.

Procedure:- In the case of the CH_2Br_2/EtBr system a 1:1 mixture was prepared by liquid volume using a micrometer syringe. This was then diluted 4:1 by volume with dimethyl phthalate and two drops injected into the chromatography via the high vacuum W-tube.

In the case of CH_2ClBr/MeBr a 1:1 mixture by gas volume was prepared. 1 cm of this was expanded into the W-tube for analysis.

A 1:1 mixture by liquid volume was prepared for the other pairs and injected through a serum cap directly into the columns.

Results:

Calibration I

Methylene bromide / ethyl bromide; 1:1 by volume ≡ 1·09:1 per mole

Run No.	$\frac{\text{Measured Area } CH_2Br_2}{\text{Measured Area EtBr}}$	$\frac{\text{Area/Mole } CH_2Br_2}{\text{Area/Mole EtBr}}$
1	1·20	1·10
2	1·22	1·12
3	1·19	1·09
4	1·22	1·11

Mean sensitivity $\frac{CH_2Br_2}{EtBr}$ = 1·11

Calibration II

Isopropyl bromide / ethyl bromide; 1:1 by volume ≡ 0·81:1 per mole

Run No.	Measured Area s-PrBr / Measured Area EtBr	Area/Mole s-PrBr / Area/Mole EtBr
5	0·83	1·02
6	0·81	1·00
7	0·83	1·02
8	0·83	1·02

Mean sensitivity $\frac{\text{s-PrBr}}{\text{EtBr}}$ = 1·02

Calibration III

t-Butyl bromide / s-butyl bromide; 1:1 by volume ≡ 0 97:1 per mole

Run No.	Measured Area t-BuBr / Measured Area s-BuBr	Area/Mole t-BuBr / Area/Mole s-BuBr
9	1·09	1·12
10	1·04	1·07
11	1·03	1·06
12	1·09	1·12
13	1·06	1·09

Mean sensitivity $\frac{\text{t-BuBr}}{\text{s-BuBr}}$ = 1·09

Calibration IV

t-Butyl bromide / isopropyl bromide; 1:1 by volume ≡ 0 84:1 per mole

Run No.	Measured Area t-BuBr / Measured Area s-PrBr	Area/Mole t-BuBr / Area/Mole s-PrBr
15	0·91	1·09
16	0·89	1·06
17	0·91	1·08
18	0·90	1·07

Mean sensitivity $\frac{\text{t-BuBr}}{\text{s-PrBr}}$ = 1·08

Calibration V

t-Butyl bromide / ethyl bromide; 1:1 by volume ≡ 0·68:1 per mole

Run No.	Measured Area t-BuBr / Measured Area EtBr	Area/Mole t-BuBr / Area/Mole EtBr
19	0·74	1·08
20	0·77	1·13
21	0·75	1·10

Mean sensitivity $\frac{\text{t-BuBr}}{\text{EtBr}}$ = 1·10

This result cross-checked with Calibrations II and III

Calibration VI

Chloro-bromo-methane / ethyl bromide; 1:1 by volume ≡ 1·17:1 per mole

Run No.	Measured Area CH_2ClBr / Measured Area EtBr	Area/Mole CH_2ClBr / Area/Mole EtBr
22	1·18	1·01
23	1·10	0·94
24	1·10	0·94
25	1·21	1·03
26	1·14	0·97

Mean sensitivity $\frac{CH_2ClBr}{EtBr}$ = 0·98

Calibration VIII

Chloro-bromo-methane / methyl bromide; 1:31 by volume ≡ 1·31:1 per mole

Run No.	Measured Area CH_2ClBr / Measured Area MeBr	Area/Mole CH_2ClBr / Area/Mole MeBr
27	1·22	0·93
28	1·21	0·92
29	1·21	0·92
30	1·17	0·89
31	1·14	0·87
32	1·24	0·95

$$\text{Mean sensivity} = \frac{CH_2ClBr}{MeBr} = 0{\cdot}91$$

The sensitivity of neopentyl bromide was assumed to be the same as t-butyl bromide because of their similar structures. No bromide was readily available for its calibration.

Summary

Bromide	EtBr	CH_2ClBr	MeBr	CH_2Br_2	s-PrBr	s-BuBr	t-BuBr	neo-PBr
Sensitivity	1	0·98	1·08	1·11	1·02	1·02	1·10	1·10

All results are relative to ethyl bromide.

7·9. Accuracy of the Work.

The statistically derived errors quoted on each result and the method of least squares were as discussed for the later fluorinations (p. 78). As for fluorination also, the systematic errors arising in pressure and analysis measurements mostly cancel by the competitive method. The absolute errors on the temperature quoted probably do not exceed $\pm\frac{1}{2}^{o}$ C. Most of these errors will be constant and only the A factors will be slightly affected.

The major source of error was traces of impurity in the reaction vessel. The effects have been discussed in individual topics. The methane / methyl chloride system was the most sensitive and errors have not been quoted. However results from attempts to brominate isopentane subsequent to Topic 7 were also extremely scattered, indicating that perhaps part of the irreproducibility, at least, was due to poor vacuum conditions arising from dirty glass in the then aged apparatus.

Attempts to compete the normal and secondary positions in propane failed because the difference in the relative rates of attack at the two positions in the same molecule was too great for accurate analysis.

CHAPTER 8.

THE REVERSE REACTION OF BROMINE HYDROGEN ABSTRACTION - RADICAL ATTACK ON HYDROGEN BROMIDE.

8·1. Previous Work.

Schumacher[71] in a comparison of the reactions of chlorine, bromine and iodine, has pointed out that the forward reaction (2) occurs more readily

$$RH + X\cdot \longrightarrow R\cdot + HX \qquad (2)$$

in the order X = Cl > Br > I. The reaction with chlorine is exothermic, while with bromine it is usually slightly endothermic and with iodine it is strongly endothermic. The situation is just the opposite for the reverse reaction (4);

$$R\cdot + HX \longrightarrow RH + X\cdot \qquad (4)$$

which is therefore of much greater importance with iodine and bromine than with chlorine and even more so fluorine. A knowledge of the activation energy of reaction (4) for bromine is of especial interest since, together with that for the forward reaction (2), it can lead to bond strength values of R-H.

Few direct measurements of (4) have been made for bromine. As has been described before, ratios of A factors and differences of activation energies of (4) and (3) were obtained in many of

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (3)$$

the bromination systems from a study of the inhibition effect of HBr. Values of E_4 were obtained on the assumption that E_3 was zero. However even for methane and hydrogen, E_3 could well have a small positive value. This together with the experimental scatter of the results makes the values almost worthless, since the possible range they give for E_4 could be evaluated by inference any way. The values obtained by this method for methyl[84] ~ 2 kcal and ethyl[90] ~ 2 kcal only may not be much in error, together with the result for hydrogen (listed in Table 9·12).

The work of Williams and Ogg[130] who photolysed hydrogen iodide in the presence of added iodine, HBr and HCl can also give E_4 for hydrogen from,

$$HI + h\nu \longrightarrow H\cdot + I\cdot$$

$$H\cdot + HI \longrightarrow H_2 + I\cdot \qquad (1)$$

$$H\cdot + I_2 \longrightarrow HI + I\cdot \qquad (5)$$

or $$H\cdot + HBr \longrightarrow H_2 + Br\cdot \qquad (4)$$

They obtained ratios of

$k_5/k_1 = 3{\cdot}5$ temperature independent

$k_1/k_4 = 0{\cdot}54 \exp(1000/RT)$.

This would lead to the result,

$k_5/k_4 = 1{\cdot}9 \exp(1000/RT)$.

E_5 was deduced by Morris and Pease[131] to be zero on the grounds that reaction (5) was 100 times faster than (1) the activation energy of which was ~ 1 keal. This would give:

$E_4 = 1$ keal.

However the results may be inaccurate because of hot radical complications. Andersen and Kistiakowsky[132] found in one experiment that:

$k_5/k_4 = 6{\cdot}3$.

They assumed zero activation energy for both (4) and (5).

Cremer, Curry and Polanyi could only give,

$E_4 < 3$ keal

from their hydrogen atom work. Steiner[134] from his ortho-para hydrogen conversion work obtained the result:

$k_4 = 10^{13} \exp(0 \pm 1800/RT)$.

All these results are listed in Table 9·12 together with other calculated values (see p. 82). A value calculated by us is also listed. The result was obtained from the mean of all the activation energies E_2 shown for the

forward reaction and a consideration of the thermochemistry:

$$\Delta H_{2,4} = E_2 - E_4.$$

The result for methane has been checked by Andersen and Kistiakowsky[132] who photolysed methyl iodide / hydrogen bromide / iodine mixtures. The methyl radicals formed in the initial step were consumed by either (6) or (7):

$$CH_3I + h\nu \longrightarrow CH_3\cdot + I\cdot$$

$$CH_3\cdot + HBr \longrightarrow CH_4 + Br\cdot \qquad (6)$$

$$CH_3\cdot + I_2 \longrightarrow CH_3I + I\cdot \qquad (7)$$

In the absence of iodine the rate of production of methane must be a maximum. The amounts of methane produced with various amounts of iodine present were compared with the maximum rate of methane production. After discounting the reaction

$$CH_3\cdot + I\cdot \longrightarrow CH_3I \qquad (8)$$

the relationship was obtained from which the ratio k_4/k_6 could be obtained:

$$\frac{\text{Rate of formation of } CH_4 \text{ in presence of iodine}}{\text{Rate of formation of } CH_4 \text{ in absence of iodine}} = \frac{k_6(HBr)}{k_6(HBr)+k_7(I_2)}$$

They considered the result of Bodenstein and Jung[75] of $k_3/k_4 = 8{\cdot}6$ for hydrogen and their own value for hydrogen of $k_5/k_4 = 6{\cdot}3$, and, on the assumption that (3), (4) and (5) had zero activation energy, inferred by analogy that

$$\frac{A_6}{A_7} = \frac{1}{7{\cdot}5}$$

From the Arrhenius equation this gave:

$$E_6 - E_7 = 0{\cdot}8 \pm 0{\cdot}3 \text{ kcal.}$$

E_7 was rather doubtfully estimated to be $0{\cdot}5 \pm 0{\cdot}5$ kcal. This gave the result

$$E_6 = 1{\cdot}5 \pm 1 \text{ kcal.}$$

Although both E_6 and E_7 seem reasonable the results are based on very hypothetical reasoning indeed.

Williams and Ogg[135] later photolysed methyl iodide in the presence of the hydrogen halides. They obtained evidence of the occurrence of hot methyl

radicals from the initial act in the presence of HCl. Methyl iodide was present in higher concentrations with HBr and was thought to deactivate the hot radicals by collision. Their results compared well with Kistiakowsky and Andersen's deduced values[132]. They obtained from the formation of methane with time

$$k_7/k_6 = 7{\cdot}5 \exp(+950/RT)$$

from rather scattered results. Thermal reaction occurred to some extent.

Shultz and Taylor[136] obtained even stronger evidence for hot methyl formation. They photolysed methyl iodide removing the iodine formed with silver vanes. Methane production was independent of iodine removal and inhibited by added CO_2. Ethane production increased rapidly as the efficiency of iodine removal increased. This indicated that methane was formed from the reaction

$$CH_3^{*} + CH_3I \longrightarrow CH_4 + CH_2I \cdot \qquad (9)$$

while ethane arose from recombination of cold methyls. A possible decrease in ethane production with increase of temperature could be accounted for by (7) having an activation energy of $\sim$ 1 kcal. Little reliance can be placed on this however because the results were strongly dependent on the vane-speed and were scattered. However the presence of hot radicals is indicated. The pressures used by these workers were higher than those of Williams and Ogg and Kistiakowsky and Andersen whose pressures were similar. This would indicate that in all three cases the results are inaccurate because of hot radical formation, although Shultz and Taylor's results may be affected by the type of radiation they used (the 2537 Å mercury line unreversed). The net result would be an underestimation of E_6. Kistiakowsky and Andersen's results may be derived from a system which is basically unsound (see p.150).

8·2. Purpose of the Present Work.

It was decided, because of the uncertainty of the activation energy values for the back reaction, to try to develop a method which would lead to more accurate results. Rather than use the iodides as a photolytic source of the alkyl radicals, the ketones were taken as being better. Hydrogen bromide and iodine introduced into the system in suitable amounts could be competed with the radicals by the following mechanism:

$$RCOR + h\nu \longrightarrow R\cdot + RCO\cdot \qquad (10)$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (11)$$

$$R\cdot + HBr \longrightarrow RH + Br\cdot \qquad (4)$$

By measuring the ratios of alkanes to alkyl iodides formed at different temperatures values of $E_4 - E_{11}$ and A_4/A_{11} could be obtained. In order to evaluate E_4 absolutely with any accuracy some direct measurement of (11) would be required. However even in the absence of this measurement the values of E_{11} obtained from previous work would not involve an error of much more than $\pm$ 0·5 kcal.

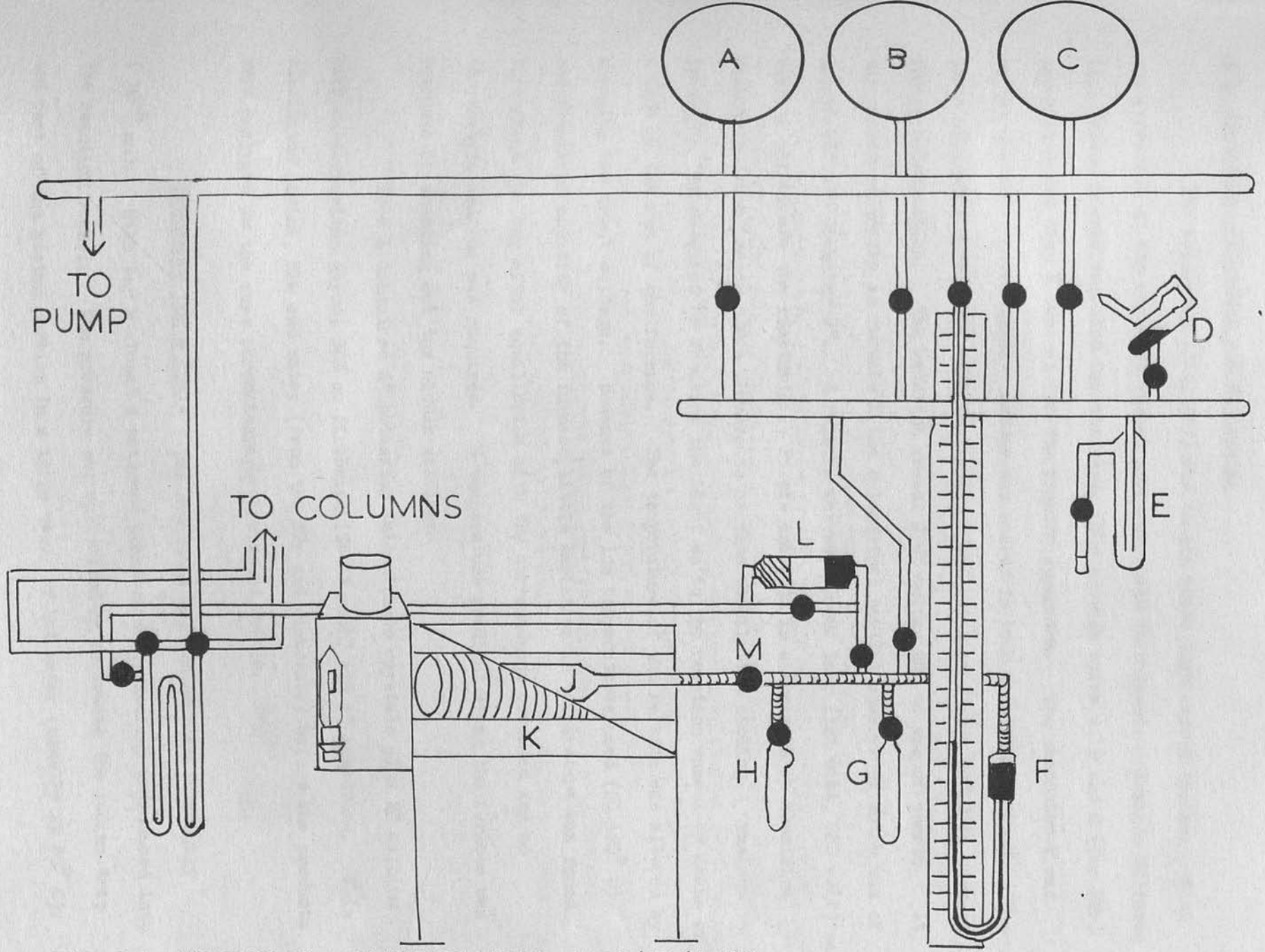


FIG. 8.1 KETONE PHOTOLYSIS APPARATUS.

8·3. Apparatus, Procedure and Materials.

The apparatus (Fig. 8·1) was an all glass, high vacuum system. With the exception of the reaction vessel, pyrex was used throughout. Edwards Silicone High Vacuum Grease was used for the taps. The storage bulbs A, B and C (for HBr) vacustat D and trap E were as for the bromine apparatus. The manometer F was of the one-limb-travel type. Ketone was stored in trap G and iodine in H. The parts indicated were wound with heating tape and maintained at ~ 90° C to prevent iodine condensation. The reaction vessel J of volume 600 cc was of quartz. It was placed centrally in furnace K, the cylindrical heating chamber of which was of length 18" and diameter 6". A Hanovia mercury vapour lamp (125 watt, 230 volt) was used to illuminate the reactants. It was enclosed in a box with an aluminium backing as a reflector and a chimney to provide ventilation cooling. Maximum intensity was obtained by focusing the light on to the reaction vessel by means of a lens on the end of the furnace. The temperature of the furnace was altered by changing the input voltage. Because of the low temperatures used (50-120° C) and the large capacity of the furnace, little variation in temperature was found throughout the day after equilibrium with the surroundings occurred and no temperature control was required. A temperature gradient along the furnace was overcome by shorting out the middle windings.

Tube L contained 3" potassium thiosulphate crystals plus 2" calcium carbonate-ethylene glycol 30% on firebrick (25-52 mesh) and 1" anhydrone. This eliminated iodine, HBr and water (from the HBr and carbonate) before the products were analysed on the same chromatography system as before.

Procedure for a Run:- The apparatus was pumped down thoroughly (10^{-5} mm). With tap M closed a measured pressure of iodine was introduced into the reaction vessel. The pressure was controlled by immersing the iodine trap and part of the heated portion in a large dewar of hot water (usually at 60° C).

About 4 cm of ketone, measured on the manometer, was then added to the iodine, the pressure being allowed to build up in the heated section first before tap M was opened so that back diffusion of the iodine was avoided. The residual ketone in the heated section was frozen back into G. HBr was introduced in a similar fashion. Its pressure was known from the total pressure and ketone plus iodine pressures read on the manometer. After illumination the reaction vessel contents were distilled through tube L to the chromatography W-trap for analysis.

Materials:

Iodine:- T. & H. Smith reagent grade was used. It was sublimed twice over KI and thoroughly degassed.

Hydrogen Bromide:- Was prepared by the action of bromine on tetralin and aluminium powder[137]. After passage through copper turnings to remove bromine, the sample was distilled from -80 to -183° C and degassed thoroughly.

Methyl Ethyl Ketone and Methyl Isopropyl Ketone:- B.D.H. samples were used after several trap (40° C) to trap (-183° C) distillations rejecting head and tail fractions.

8·4. Results.

Topic No. 2. Photolysis of Methyl Ethyl Ketone-Hydrogen Bromide-Iodine Mixtures.

Mixtures of methyl ethyl ketone, hydrogen bromide and iodine were photolysed over the temperature range 51-114·5° C analysing mainly for ethane and ethyl iodide.

Chromatography:- Split columns were used. Ethane was analysed on 3' celite (80-100 mesh) / 20% diethyl phthalate at 35° C plus 2½' alumina (40-60 mesh) at 0° C. Ethyl (and methyl) iodides were measured on the celite alone by by-passing the alumina with a two-way tap after the ethane had been recorded. A flow rate of 50 cc/min eluted ethane under these conditions in 2½ min, methyl iodide in 6 min and ethyl iodide in 12 min. Methane could not be analysed on these columns.

Reactant Pressures:- All pressures are recorded in Table 8·1. Variation of the iodine, ketone and HBr pressures by a factor of two had no effect.

Illumination:- Because of the large capacity of the reaction vessel and the illumination set-up the time required was very short (~5 min) to give enough product (5 μmole) for analysis. In Run 10 a pyrex shield was placed in front of the lamp limiting the spectrum to wavelengths >3,000 Å. This had no effect on the result although the reaction was three times slower.

The runs at lower temperatures were scattered and, because of the small temperature range, a further check will be necessary to obtain the accuracy required. Consequently the results have not been given a least squares' treatment but the best line through the mean points drawn. The results are shown in Table 8·1 and the Arrhenius plot of the mean points in Fig. 8·2.

Result:

$$k_{EtI}/k_{Et} = 1{\cdot}58 \exp (2065/RT).$$

Table 8.1. Results of Methyl Ethyl Ketone Photolysis

Run No.	Temp° K	I_2(mm)	HBr(cm)	Ketone (cm)	k_{EtI}/k_{Et}
18	327.5	2.24	4.20	4.95	39.93
20	332	3.24	4.67	4.85	36.05
46	338	4.57	4.54	4.31	32.28
21	345.5	"	4.34	4.60	35.14
23	346.5	"	3.63	4.55	31.77
24	"	"	3.01	4.72	28.70
26	347.5	"	3.60	4.85	31.11
28	361	"	4.79	5.16	26.47
31	"	"	3.58	6.62	26.98
41	360.5	"	4.28	4.26	24.97
42	"	"	4.74	4.42	30.15
43	362	3.24	5.56	3.87	27.05
44	"	4.57	6.03	3.15	28.27
45	"	"	3.29	3.30	26.83
33	374.5	"	3.81	4.57	25.24
34	"	"	3.70	4.67	24.71
9	392.5	"	4.48	4.82	23.66
10	"	"	4.75	5.45	21.99
37	387.5	"	4.24	2.84	20.93
38	"	"	4.90	4.25	22.91
39	"	"	4.76	4.36	22.80
40	"	"	4.70	5.05	22.35

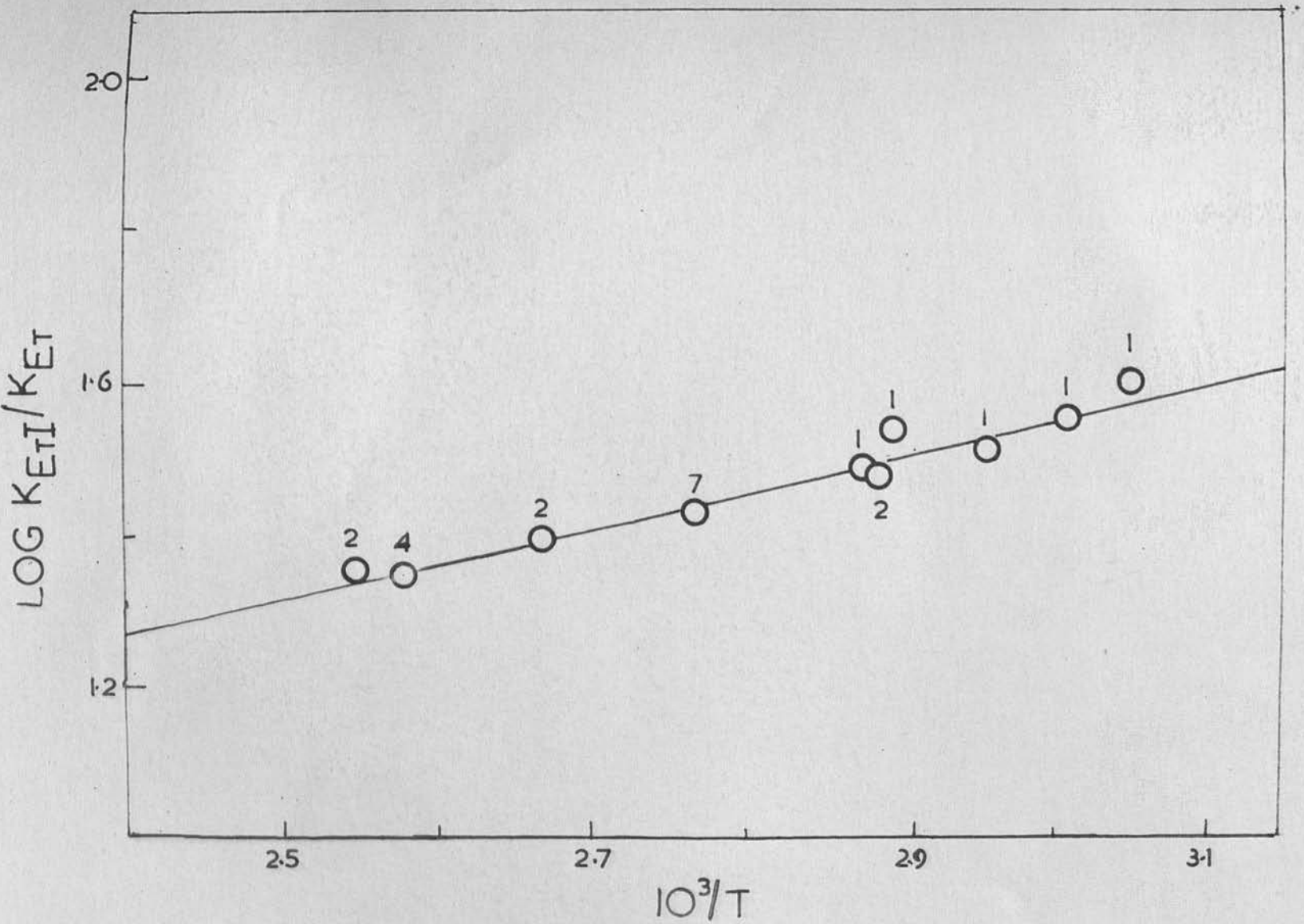


FIG. 8.2. PLOT OF MEAN POINTS.

8·5. Discussion of the Ketone Photolysis.

Although the method has not been thoroughly investigated and one topic only has been completed to give quantitative results, the system is extremely interesting and holds numerous possibilities. Some qualitative deductions can be made which, although they are not directly connected to the main reason for this branch of the work (namely the determination of the activation energy for the back reaction), merit some discussion.

Firstly the system itself must be considered. Reactions other than (10), (11) and (4) are possible. Reaction (12) will almost certainly occur but will not affect the results.

$$RCO\cdot + I_2 \longrightarrow RCOI + I\cdot \qquad (12)$$

Photolysis of the iodide product could occur with the wavelengths used:

$$RI + h\nu \longrightarrow R\cdot + I\cdot \qquad (13)$$

However, even if this occurred with 5% of the total iodide, the effect on the results would not be large since it would be followed by,

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (11)$$

at least 4 times faster than,

$$R\cdot + HBr \longrightarrow RH + Br\cdot \qquad (4)$$

after allowance for the relative pressures of HBr and iodine. Photolysis of HBr is a more serious possibility for some light of wavelengths < 2537 Å (where HBr begins to absorb) must certainly have been used. The bromine atoms resulting from (14) would probably react with the ketone.

$$HBr + h\nu \longrightarrow H\cdot + Br\cdot \qquad (14)$$

If however attack on the products occurred the iodide would possibly be depleted more than the alkane, but the effect would be difficult to forecast. The reactive hydrogen atoms, too, might attack the iodide. When the methyl ethyl ketone and HBr were photolysed alone, ethane was formed only in small amount from the reaction

$$C_2H_5\cdot + C_2H_5COCH_3 \longrightarrow C_2H_6 + \cdot CH_2CH_2COCH_3 \qquad (15)$$

However it would not have affected the ratios of rate constants by more than 2% under the most adverse conditions. For more accurate work a correction could be made.

The results of the methyl ethyl ketone photolysis are sufficiently consistent and independent of reaction conditions to indicate the system is clean and no side reactions occurred to an important extent.

Although no absolute measurements of quantum yields were made, there was a strong indication for both ketones that the amount of product formed in a fixed time with constant illumination in the presence of iodine was less than in its absence, i.e. the quantum yield of the initial act was less. The presence of iodine could well lower the efficiency of the initial act in the photolysis of methyl iodide, so that Kistiakowsky and Andersen's comparison of the rate of methane formation in the presence and absence of iodine would be invalid.

At the lower temperatures with methyl ethyl ketone the ratio of methyl iodide / ethyl iodide was small (1:40 at 60° C), and could not be counterbalanced by hydrocarbon formation. This means that the reaction,

$$C_2H_5COCH_3 + h\nu \longrightarrow C_2H_5\cdot + CH_3CO \qquad (16)$$

occurs more readily than,

$$C_2H_5COCH_3 + h\nu \longrightarrow CH_3\cdot + C_2H_5CO \qquad (17)$$

The work of Pitts and Blacet[138] and Martin and Sutton,[139] who found that at 100° C and 3,130 Å in the photolysis of methyl ethyl ketone with iodine the ratio ethyl iodide/ methyl iodide = 20-40:1, is in support of such a mechanism. The ratio fell at shorter wavelengths. Also, as was found here in a run with the same ketone and iodine, almost all their products were iodides which eliminates the possibility of an initial molecular reaction.

When methyl ethyl ketone was illuminated for the same time (20 min) as the methyl isopropyl ketone the same amount of methyl iodide was formed in both

cases, whereas three times as much ethyl iodide plus ethane as propane plus propyl iodide were formed. Reactant pressures and conditions were similar. Since the quantum yields of methyl iodide are the same in both cases the formation of isopropyl radicals must be slower than ethyl radicals, unless the rate of

$$CH_3CO \longrightarrow CH_3\cdot + CO \cdot \qquad (18)$$

is different in both cases. This is unlikely unless in the initial act $CH_3CO\cdot$ is formed with more energy in the case of the isopropyl ketone, despite less initial absorption by that ketone which would have to occur.

Again assume the isopropyl ketone absorbs less in the presence of iodine than the ethyl ketone but that a molecular reaction occurs which produces a product to give, on photolysis, methyl radicals; the isopropyl radical yield would be less than the ethyl radical yield, but the methyls could be the same in both cases. Methyl n-propyl ketone has been found to give acetone and ethylene by a molecular reaction. Methyl n-butyl ketone yields propylene and acetone while methyl s-butyl ketone has been reported to give ethylene and methyl ethyl ketone as major products[140]. If ethylene and acetone were formed by a molecular reaction from methyl isopropyl ketone, photolysis of the acetone could perhaps maintain the methyl yield. If however this did not occur, the similar quantum yields of methyl iodide in both ketone photolyses would indicate that since no molecular reaction occurred with methyl ethyl ketone, none occurred with methyl isopropyl ketone either. Unfortunately ethylene could not be measured to test this theory.

Why then the lower propyl iodide quantum yield? Although other products were formed, they were not in sufficient amount to indicate the occurrence of side reactions as the sole reason. It could be argued that while the production of methyls from the reactions,

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO \qquad (18)$$

$$RCOCH_3 \longrightarrow CH_3\cdot + RCO\cdot \qquad (19)$$

or even,

$$RCOCH_3 \longrightarrow R^{\cdot} + CO + CH_3^{\cdot} \qquad (20)$$

occurs equally well for both ketones the reaction,

$$CH_3COC_3H_7 \longrightarrow C_3H_7^{\cdot} + CH_3CO^{\cdot} \qquad (21)$$

occurs less readily than,

$$CH_3COC_2H_5 \longrightarrow C_2H_5^{\cdot} + CH_3CO^{\cdot} \qquad (16)$$

A stronger possibility is the formation of propylene (which could not be measured) rather than the propyl iodide. Elimination of HI from the iodide is the most probable mechanism for this to occur. Break-down of the isopropyl radical is also possible. Isomerization of the isopropyl iodide was certainly strongly indicated, which is a little surprising since the isopropyl should be slightly more favoured than the n-propyl isomer on thermochemical grounds. However such a reaction has been reported previously by Glazebrook and Pearson[141] who photolysed di-isopropyl ketone, converting the radicals formed into the propyl mercuric bromides and iodides. They identified n-propyl mercuric bromide and iodide rather than the isopropyl compounds. They thought that either spontaneous isomerization of the isopropyl radical occurred or else the isomerization occured during the formation of the halide, which is more likely. The same could apply to our iodide.

CHAPTER 9.

GENERAL DISCUSSION OF HALOGEN HYDROGEN ABSTRACTION RESULTS

9·1. Rate Constants - Ratios.

Comparisons can be made of some of the rate constant ratios found in this work for hydrogen abstraction by bromine and fluorine atoms in reaction (2) with those of other workers.

$$X\cdot + RH \longrightarrow R\cdot + HX \qquad (2)$$

Although Anson, Fredricks and Tedder[36] did not determine any temperature coefficients for bromination, the ratios of the rate constants for the butanes obtained by them may be compared with ours. At 146° C their results were:

$$k_{sn\text{-}Bu}/k_{pn\text{-}Bu} = 82$$

and $k_{t.isoBu}/k_{pn\text{-}Bu} = 1640$.

Our results at 146° C give:

$$k_{sn\text{-}Bu}/k_{Et} = 143$$

and $k_{t.isoBu}/k_{Et} = 1820$.

The discrepancy between k_s/k_p is outside experimental error. Since our value of $k_{t.isoBu}/k_{Et}$ was obtained from $k_{t.isoBu}/k_{sn\text{-}Bu}$ and $k_{sn\text{-}Bu}/k_{Et}$ it is surprising that the k_t/k_p values agree so well. However our value at 146° C of

$$k_{sPr}/k_{Et} = 85$$

does compare with Tedder's k_s/k_p value. Fredricks and Tedder[38] also found that the attack of bromine at the 1-position in n-butyl chloride was 34 times faster than the attack at a primary hydrogen in n-Butane at 146° C. Our value at 146° C of

$$k_{MeCl}/k_{Me} = 50$$

is in as close agreement as could be expected.

Ratios of rate constants for fluorination can be compared with the work of Anson, Fredricks and Tedder[36] who found at 298° C,

$k_{pn\text{-}Bu}/k_{sn\text{-}Bu} = 1{\cdot}20 \pm 0{\cdot}17$

and $k_{pisoBu}/k_{tisoBu} = 6{\cdot}47 \pm 0{\cdot}70$.

Our results at 298° C for the same ratios are respectively $1{\cdot}30 \pm 0{\cdot}09$ and $6{\cdot}41 \pm 0{\cdot}34$. The agreement is excellent.

Absolute Rate Constants:- Unfortunately no previous absolute rate constant measurements have been made for fluorine hydrogen abstraction reactions. The rate of the reaction and effect of heterogeneity makes the task a formidable one indeed. However in the case of bromine several reliable measurements have been made. Although their discussion is a little premature here since comparison with our values requires the derivation of A factors and activation energies which is done later, they are discussed here and tabulated later (Table 9·12.). This then enables a discussion of the accuracy of our system.

The bromination activation energy differences and A factor ratios obtained in this work have been related to the absolute activation energy and A factor found by Kistiakowsky and Van Artsdalen[84] for methyl bromide to give a series of absolute values. Since the errors in the ratios and differences are small, the results should be accurate provided the methyl bromide result is reliable. Although in fact Kistiakowsky's result for methane would have perhaps been a better standard, our results for methane were not too accurate for the reasons given previously. There is little loss in accuracy in taking methyl bromide especially in view of the conclusions of Benson and Buss[97]. The rate constants at 100° C derived from these absolute Arrhenius parameters are listed in Table 9·12 with those from other bromination work. Our value for methane is higher than Kistiakowsky's by a factor of two. Although we had hoped for better agreement the difference is not too large, especially since methyl bromide and methane are related to each other in our system through three rate constant ratios. Our result for isobutane, however, is lower by a factor of 10^2 than the value obtained by Van Artsdalen and co-workers. It is

to be noted that 100° C is higher than the temperature scale (40-95° C) over which the isobutane bromination was investigated. While the other workers' result for neopentane is only higher by a factor of three than ours, 100° C here is at the lower end of their temperature scale (98-152° C) and, since their activation energy is higher than ours, their rate constant will diverge from ours at higher temperatures.

According to the arguments of Benson and Buss[97], the abnormally high values of especially the A factors for the hydrogen abstraction reaction of bromine on several of the substrates including neopentane and isobutane were due to the thermal reaction being studied under non-stationary state conditions arising because of the long induction period for bromine dissociation. This, according to them, resulted in heterogeneous reaction at the walls and recombination by $R^{\bullet} + Br^{\bullet}$ and/or $R^{\bullet} + R^{\bullet}$ rather than $Br^{\bullet} + Br^{\bullet} + M$, as a result of a high value for the ratio $R^{\bullet}/Br^{\bullet}$. These criticisms must be discussed in respect to our system. Firstly the recombination effect which is controlled by θ which is given by:

$$\theta = R/Br \simeq k_2/k_3 \times (RH)/(Br_2)$$

where k_3 is the rate constant of

$$R^{\bullet} + Br_2 \longrightarrow RBr + Br^{\bullet} \qquad (3)$$

Calculation shows that in the worst case θ was never $> 10^{-2}$ at which value the recombination effect should only be slight. Both k_2 and $(RH)/(Br_2)$ were lower in our case than in the other workers'. As was seen in the discussion of the competitive method, although the concentration of the halogen atoms does not in itself affect the results, the fate of the radical $R^{\bullet}$ is important. Recombination by $R^{\bullet} + X^{\bullet}$ would give the same result as $R^{\bullet} + X_2$ and $X^{\bullet} + X^{\bullet}$. Recombination by $R^{\bullet} + R^{\bullet}$ would however alter the results. No measurable amounts of the dimers RR were found and if they had been, suitable corrections could have been made. The recombination effect does not invalidate our system, therefore.

The occurence of heterogeneity is not so easy to discount. However it

must be remarked that our values for the Arrhenius parameters, unlike those of the previous workers for neopentane and isobutane are reasonable and indeed, as will be seen later, appear to be extremely accurate. If heterogeneity had occurred such results would not have been expected. Precautions were taken to avoid such effects. The bromine was preilluminated for three minutes by itself in the reaction vessel prior to the introduction of the hydrocarbon, since the induction period, according to Benson and Buss, is much smaller for the photochemical dissociation of bromine. In the absence of such a precaution the results obtained tended to show the effects of less rather than more heterogeneity. Moreover, the random variation in the length of the runs and intermixing of thermal and photochemical reactions which was practised at each temperature had no effect on the results. Finally the systems studied were arranged so that the rate of formation of product from the two hydrocarbons in a pair rarely differed by a factor of ten. Under these conditions the recombination and heterogeneous effects should cancel to some extent at least.

We have still to explain why the rate constants of Van Artsdalen and co-workers in Table 9·12 are higher than ours and why they become even higher as the temperature is raised. Although they are derived from the photobromination activation energies and thermal A factors, the chief source of error is probably the thermal reaction. Although the reason may be partly reaction under non-stationary state conditions with the occurence of other recombination reactions according to Benson and Buss, there is no convincingly positive evidence for heterogeneous reaction. Some other factors may be involved.

Effect of Hydrogen Bromide:- The addition of hydrogen bromide equivalent to the amount formed during a normal run has been proved to have no effect on the results. The addition of twenty times that normally formed only had a small effect. This is probably because the concentration of hydrogen bromide relative to

bromine at the end of a run was still very small (1:50). Also, since by the competitive method ratios of rates were being measured, the effects of hydrogen bromide would tend to cancel.

Intercomparison of Halogen Rates:- In order to obtain a comparison with fluorine for attack on different hydrogen types the rate constants per hydrogen relative to ethane for fluorine, bromine and chlorine hydrogen abstraction at 25° C have been listed in Table 9·1. Absolute rate constants for bromine and chlorine at 25° C are also included. It is noticeable that while the rate constants relative to ethane for bromine and chlorine attack on hydrogen and methane are similar, attack of fluorine is much slower for hydrogen than methane. Mercer and Pritchard's relative rate[43] for hydrogen may be low or our result for methane high, or both. While the rate constants for attack at the primaries relative to ethane decrease with increase in chain length and chain branching for fluorine, there is a tendency to increase for chlorine. Insufficient results of primaries are available to make generalisations for bromine. The selectivity of the halogens increases in the order F<Cl<Br. Bromine is very much more selective than the other two. The relative rates of attack at the different types of hydrogen is usually in the order tertiary>secondary>primary>halides>methane. Fluorine attack on the secondary in n-butane and both chlorine and fluorine attack on cyclopropane appear to be exceptions to this rule. The absolute rate constants for chlorine are very much higher than the corresponding results for bromine. Those for fluorine will be slightly higher than for chlorine.

Table 9·1. Halogen Rate Constants and Rates Relative to Ethane for Reaction (2)

Bond Type RH	$\frac{k_{RH}\ (25°\ C)}{k_{Et}}$			k (25° C) mole^{-1} cm^3 sec^{-1}	
	Bromine	Fluorine	Chlorine	Bromine	10^{-13} x Chlorine^2
H_2	1.10×10^{-3}	0.67[43]	1.4×10^{-3}	2.19	3.6×10^{-4}
CH_4	0.53×10^{-3}	0.81	3.6×10^{-3}	1.05	0.9×10^{-3}
Primary C-H bonds					
C_2H_6	1.00	1.00	1.00	2.00×10^3	0.26
C_3H_8	-	0.88	1.24	-	0.31
n-C_4H_{10}	-	0.79	1.48	-	0.37
IsoC_4H_{10}	-	0.83	1.28	-	0.33
NeoC_5H_{12}	2.50×10^{-1}	0.76	1.16	5.01×10^2	0.30
Secondary C-H bonds					
CycloC_3H_6	-	0.78	3.2×10^{-3}	-	0.8×10^{-3}
C_3H_8	4.67×10^2	1.06	4.56	9.33×10^5	1.14
n-C_4H_{10}	0.66×10^3	0.91	5.60	1.37×10^6	1.40
Tertiary C-H bond					
IsoC_4H_{10}	3.12×10^4	1.17	6.64	6.24×10^7	1.64
Halides					[42]
CH_3Cl	1.78×10^{-1}	-	6.2×10^{-2}	3.55×10^2	1.6×10^{-2}
CH_3Br	1.51×10^{-2}	-	-	3.02×10	-

The rate constants listed are for individual hydrogen atoms of the specified type.

9·2. A. Factors.

Theory of Interpretation:- The early theory of reaction rates, namely the simple collision theory, although it gave a roughly correct crude picture of how a bimolecular reaction went, did not give the complete answer. The simplest collision theory was based on the frequency of collision between two rigid spheres (the reactants). Only those collisions led to reaction where the sum of the energies of the two colliding species exceeded E, the activation energy. Energy in only two degrees of freedom was considered, namely the components of energy of translation of each of the species along the line of centres at the time of collision. Large discrepancies between the predicted and experimental A factors often occurred. As a consequence the theoretical equation was often written in the form,

$$k = pZe^{-E/RT}$$

where p was a measure of the discrepancy between the simple collision theory and experimental results. Although more complex expressions have been developed most workers who have based their results on the collision theory have used the simple expression. It should be noted in this respect that the theory predicts a $T^{\frac{1}{2}}$ temperature dependence of the A factor and a consequent term in the activation energy. The equation is in the form,

$$k = BT^{\frac{1}{2}}e^{-H/RT}$$

The results expressed in this manner have all been converted in this work into the normal Arrhenius parameters. The formulation of the theory may be found elsewhere[142] and is not given here. The development of the transition-state theory, where the reaction is interpreted as proceeding via an intermediate activated complex, revealed the essential defect of the collision theory is its neglect of internal degrees of freedom. Its treatment of the reactants as rigid spheres rather than an assembly of nuclei and electrons was oversimplified. The collision theory is a special case of the transition-state theory. A formal development of the transition-state equation is given elsewhere.[143] The equation is,

$$k = e^{-(\Delta n^{\ddagger}-1)}.kT/h.e^{\Delta S_c^{\ddagger}/R}.e^{-E \exp/RT}$$

where $\Delta n^{\ddagger}$ is the increase in the number of molecules when the activated state is formed from the reactants and $\Delta S_c^{\ddagger}$ is the change of entropy in the formation of the activated complex with unit concentration as the standard state. For a bimole-

cular reaction $\Delta n^{\ddagger} = -1$. E exp is the experimental activation energy obtained from the Arrhenius relationship. The Arrhenius A factor for a bimolecular reaction is then given by,

$$A = e^2 \frac{kT}{h} e^{\Delta S_c^{\ddagger}/R}$$

Thus the terms in which the A factors are formulated in the transition-state theory, unlike in the collision theory, all have a theoretical significance. The accuracy of the theory is limited however by our inadequate knowledge of the activated complex. Accurate experimentally found A factors would enable such information to be obtained. This was one of the reasons for carrying out the researches on the hydrogen abstraction reactions of the halogens since, being simple reactions, they offered a good testing ground for the transition-state theory.

Experimental A Factors for the Hydrogen Abstraction Reaction:- The ratios of experimental A factors obtained for bromine hydrogen abstraction reactions are shown in column 2 in Table 9·2. These ratios differ slightly from those given in the experimental section since they have been corrected for the small differences shown by the thermal conductivity gauge in the measurements of the bromides (p.138). It is easier to correct the final result than all the individual rate constant ratios. The corrected ratios so obtained direct from the Arrhenius plot are molecular ratios, i.e. they do not take into account the type or number of hydrogens present on each molecule. The ratio per hydrogen is obtained by multiplication by the inverse ratio of the number of hydrogens of a given type present in the two hydrocarbons being attacked. These results are shown in column 3 of Table 9·2. Similar results for fluorine are shown in columns 2 and 3 of Table 9·3 along with the result for the methane-hydrogen system obtained by Mercer and Pritchard[43]. Only the ethane / methane ratio has had to be corrected here for the different elution sensitivity of methyl fluoride.

Table 9·2. Bromination Experimental A Factor Ratios and Activation Energy Differences

Mixtures Brominated $R_1H + R_2H$	$\frac{A_2R_1H}{A_2R_2H}$ per molecule	$\frac{A_2R_1H}{A_2R_2H}$ per H atom	$E_2R_2H-E_2R_1H$ cal. mole^{-1}
$ClCH_2$-H + CH_3-H	0·400	0·530	3799
C_2H_5-H + $ClCH_2$-H	1·897 ± 0·109	0·948 ± 0·055	1055 ± 44
C_2H_5-H + $BrCH_2$-H	1·473 ± 0·122	0·736 ± 0·0 61	2654 ± 88
secC_3H_7-H + C_2H_5-H	0·656 ± 0·053	1·968 ± 0·159	3247 ± 51
neoC_5H_{11}-H + C_2H_5-H	2·235 ± 0·117	1·118 ± 0·059	-893 ± 44
tert.isoC_4H_9-H + secC_3H_7-H	0·390 ± 0·040	0·780 ± 0·080	2640 ± 65
tert.isoC_4H_9-H + sec n-C_4H_9	0·121 ± 0·009	0·483 ± 0·034	2716 ± 30

Table 9.3. Fluorination Experimental A Factor Ratios and Activation Energy Differences

Mixtures Fluorinated $R_1H + R_2H$	$\frac{A_{2}R_{1}H}{A_{2}R_{2}H}$ per molecule	$\frac{A_{2}R_{1}H}{A_{2}R_{2}H}$ per H atom	$E_{2}R_{2}H-E_{2}R_{1}H$ cal.mole.$^{-1}$
$CH_3-H + H-H$[43]	1.05	0.53	500 ± 200
$C_2H_5-H + CH_3-H$	0.38 ± 0.04	0.26 ± 0.03	928 ± 41
C_2H_5-H + pri.C_3H_7-H	1.84 ± 0.05	1.84 ± 0.05	-279 ± 12
pri.C_3H_7-H + pri.n-C_4H_9-H	1.11 ± 0.06	1.11 ± 0.06	0
sec.C_3H_7-H + sec.n-C_4H_9-H	0.56 ± 0.04	1.12 ± 0.08	0
pri.isoC_4H_9-H + pri.n-C_4H_9-H	1.57 ± 0.06	1.05 ± 0.04	0
neo$C_5H_{11}H$ + pri.isoC_4H_9-H	1.22 ± 0.04	0.92 ± 0.03	0
pri.n-C_4H_9-H + cycloC_3H_5-H	1.02 ± 0.06	1.02 ± 0.06	0
sec.n-C_4H_9-H + cycloC_3H_5-H	0.80 ± 0.06	1.20 ± 0.09	0
pri.C_3H_7-H + cycloC_3H_5-H	1.13 ± 0.15	1.13 ± 0.15	0
sec.C_3H_7-H + cycloC_3H_5-H	0.45 ± 0.05	1.35 ± 0.15	0
pri.C_3H_7-H + sec.C_3H_7-H	2.48 ± 0.08	0.83 ± 0.03	0
pri.n-C_4H_9-H + sec.n-C_4H_9-H	1.30 ± 0.09	0.87 ± 0.06	0
pri.isoC_4H_9-H + tert.isoC_4H_9-H	6.41 ± 0.34	0.71 ± 0.04	0

Table 9·4. Experimental A Factors for Fluorine, Bromine and Chlorine Atom Hydrogen Abstraction Reactions.

Bond Type RH	log A_2 cm^3 mole^{-1} sec^{-1} Fluorine	Bromine	Chlorine[2]
		[43] [73,81]	
H_2	13·76	13·9	13·60
CH_4	13·49	13·42	12·78
Primary C-H bonds			
C_2H_6	12·90	13·12 ± 0·04	13·18
C_3H_8	12·64	-	13·23
n-C_4H_{10}	12·59	-	13·15
IsoC_4H_{10}	12·61	-	13·11
NeoC_5H_{12}	12·58	13·17 ± 0 06	13·15
Secondary C-H bonds			
CycloC_3H_6	12·59	-	12·95
C_3H_8	12·71	13·41 ± 0·07	13·56
n-C_4H_{10}	12·67	13·62 ± 0·14	13·34
Tertiary C-H bonds			
IsoC_4H_{10}	12·76	13·30 ± 0·11	13·23
Halides			
CH_3Cl	-	13·14 ± 0·06	13·49[42]
CH_3Br	-	13·25[84]	-

The A factors listed are for individual hydrogen atoms of the specified type.

The logarithms of the absolute bromine A factors per hydrogen listed in Table 9·4 have been derived using the absolute value of log A = 12·50 per hydrogen obtained by Kistiakowsky and Van Artsdalen for the reaction:

$$Br\cdot + CH_3Br \longrightarrow HBr + BrCH_2\cdot$$

The reason for this choice was given previously (p.154). A reasonably good approximation to the absolute fluorine A factor values was obtained by taking the calculated A factor for ethane (log A = 12·90, see Table 9·5) as being equivalent to the absolute experimental value. The results for hydrogen, having been done by the consumptive method, were not very accurate and therefore were not used, although they normally would have been a better standard. The values obtained have been listed in Table 9·4. For comparison the chlorine A factors obtained by Knox and Nelson have also been listed.

The A factors for all three halogen atoms show similar trends. Those for attack at the primary hydrogens are fairly constant, apart from the cases of hydrogen and methane which cannot be regarded as having true primary bonds. The A factors for hydrogen are at least a factor of three higher than the normal primary positions for all three halogens. While methane lies intermediate between hydrogen and the primaries for fluorine and bromine the figure for chlorine is the lowest result recorded for that halogen which casts doubts on its validity. The fluorine A factor for ethane is higher than for the other primaries. The A factors for the secondary positions in the straight chained alkanes, although not as constant as the primaries, do tend to be slightly higher than the primaries. The bromine result for sec. n-butane is higher than for all the other substrates apart from hydrogen, while with fluorine it is lower than the primary in ethane. It is however higher than that for the primary in n-butane. The chlorine and fluorine A factors for cyclopropane are lower than for the other secondary positions and are nearer the lowest results for the primaries. While the fluorine A factor for the tertiary hydrogen in isobutane is higher than the secondaries in other

hydrocarbons but still lower than for methane, hydrogen (and ethane), the results for chlorine and bromine tend to be intermediate between the primaries and secondaries. The bromine A factors for the halides resemble those for primary bonds, while the result for chlorine atom attack on methyl chloride is nearer the secondary values.

The fluorine A factors are not on a true absolute scale and the chlorine results may be slightly high due to the experimental value for chlorine atom abstraction from hydrogen, which was taken as the absolute standard, being investigated on a higher temperature scale than the bulk of the chlorinations. Intercomparison of the absolute values may be uncertain therefore. It does appear, however, that the experimental A factors for chlorine and bromine atom hydrogen abstraction are similar in most cases and are higher than those for fluorine atoms.

Calculation of A Factors:- Knox and Trotman-Dickenson[144] attempted to correlate the known relative A factors for chlorine atom reactions with calculated values using the equation,

$$\frac{A_{R_aH}}{A_{R_bH}} = \left\{\frac{M_{R_aHCl}/M_{R_aH}}{M_{R_bHCl}/M_{R_bH}}\right\}^{3/2} \times \left\{\frac{(ABC)_{R_aHCl}/(ABC)_{R_aH}}{(ABC)_{R_bHCl}/(ABC)_{R_bH}}\right\}^{1/2}$$

where Ms are molecular weights and (ABC) is the product of the moments of inertia about the three principal axes of the molecules. No account was taken of vibrational entropy terms and the discrepancies between experimental and calculated A factors were serious. The method of calculation has been extended[2,145,146]. An outline of the method is given below.

The entropy term in the expression for the A factor of a bimolecular reaction given before may be expanded to give,

$$A = e^2 \, kT/h \exp\left[(\Delta S^{\ddagger}_{tr} + \Delta S^{\ddagger}_{rot} + \Delta S^{\ddagger}_{vib})/R\right]$$

where the three $\Delta S^{\ddagger}$ terms are respectively the changes in translational, rotational and vibrational entropies in the formation of the activated complex from the

reactants. The translational entropy of activation at 298° K, the temperature chosen, for

$$RH + X\cdot \rightleftharpoons RHX \longrightarrow R\cdot + HX \qquad (2)$$

is given exactly by:

$$\Delta S^{\ddagger}_{tr} = 1{\cdot}5R\ln(M^{\ddagger}/M) - S_{tr}X \text{ cal.mole}^{-1}\text{deg}^{-1}$$

where $M^{\ddagger}$ and M are the molecular weights of RHX and RH respectively and the standard state is 1 mole cm^{-3}. S_{tr} for X = F is 14·75 while for Br it is 19·02 cal.$mole^{-1}deg^{-1}$

The rotational entropy of activation can be obtained from:

$$\Delta S^{\ddagger}_{rot} = 0{\cdot}5R\ln(A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHX and RH. This value is for reaction at a single hydrogen atom of any type; inclusion of the symmetry number in the expression would yield $\Delta S^{\ddagger}_{rot}$ appropriate to all the hydrogens of a given type in the molecule. The ABC values can be evaluated graphically with sufficient accuracy by assuming suitable configurations and bond lengths in RH and RHX. C-H and C-C distances were taken as 1·10 and 1·54 Å except for the half order bonds in the complexes, i.e. the $\rightarrow C\cdots H\cdots X$ bonds. After Pauling they were assumed to be 0·18 Å longer than the corresponding single bonds giving,

$C\cdots H$ = 1·28 Å, $H\cdots Br$ = 1·59 Å and $H\cdots F$ = 1·10 Å.

All bond angles were taken as tetrahedral with the exception of the C-H-X cases which were taken as 180°. It was found that the results depended little on the dimensions of the complex and the errors arising in the totational entropy term were small.

The calculation of the vibrational entropies of activation was much less certain. It was assumed that most of the molecular motions in the complex would be the same as those of the reactant substrate and so they were disregarded in calculating the change of vibrational entropy. Only those vibrations most intimately associated with the site of reaction should be greatly altered. The alterations

would be similar for the members of a series such as the paraffins. It was assumed that the only new vibrations that had to be considered were the symmetrical stretching and doubly degenerate bending of R-H-X bonds. It was thought that this simplification might have introduced an error into the absolute values calculated for the A factors but should have little effect on the accuracy of the relative A factors calculated for different members of a series. The frequencies of the bending and stretching motions were derived from the values used by Pitzer[147] for the probably bending and stretching frequencies for the H_2Cl complex. Pitzer's calculation of the bending vibration of this complex was based on the value for the stretching frequency derived by Bigeleisen and Wolfsberg[148]. The force constants for these frequencies were assumed to be unaffected by a change in R. The frequencies for the other complexes were than obtained from considerations of the masses of R, H and Br and their internuclear distances. The corresponding entropies were obtained from tables.

The results for the calculations at 298° K for fluorine and bromine atoms are shown in Table 9·5 with the inclusion of the results for chlorine for comparison. The values for bromine atom abstraction from hydrogen and isobutane may be compared with values calculated by Wilson and Johnston[149] for these reactions. They derived their frequencies from calculated bending and stretching force constants for the bonds of the activated complexes. They also took into account small changes in the original vibrations of the hydrocarbons. Their value for the reaction of hydrogen (log A calc = 14·1) was similar to, and for isobutane (log A calc = 12·4) lower than, the values obtained by Knox and Trotman-Dickenson[146].

A comparison between experimental and calculated A factors is shown also in Table 9·5 by listing the values of log (A exp/A calc). It is apparent that the differences between the experimental and calculated results are small for all three halogens. The variation of these differences with the type of hydro-

Bond Type RH	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$
	⟵		⟵ $Cl\cdot + RH^2$	⟶
	⟶			
H_2	76[43]	+0·54	13·60	+0·23
CH_4	49	+0·29	12·78	-0·68
Primary C-H bon				
C_2H_6	90	0·00	13·18	-0·10
C_3H_8	64	-0·05	13·23	+0·25
$n\text{-}C_4H_{10}$	59	-0·03	13·15	+0·20
$isoC_4H_{10}$	61	+0·04	13·11	+0·24
$neoC_5H_{12}$	58	+0·06	13·15	+0·31
Secondary C-H b				
$cycloC_3H_6$	59	-0·17	12·95	-0·16
C_3H_8	71	-0·03	13·56	+0·52
$n\text{-}C_4H_{10}$	67	+0·08	13·34	+0·50
Tertiary C-H bo				
$isoC_4H_{10}$	76	+0·15	13·23	+0·41
Halides				
CH_3Cl	-	-	13·52[42]	-0·29
CH_3Br	-	-		

Table 9·5 A Factors for Bromine, Chlorine and Fluorine Atom Reactions.

Bond Type RH	Br· + RH → $\Delta S^{\ddagger}_{tr}$ +19·02	$\Delta S^{\ddagger}_{rot}$	$\Delta S^{\ddagger}_{vib}$	log A (calc)	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$	F· + RH → $\Delta S^{\ddagger}_{tr}$ +14·75	$\Delta S^{\ddagger}_{rot}$	$\Delta S^{\ddagger}_{vib}$	log A (calc)	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$	Cl· + RH^2 → log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$
H_2	11·05	6·85	1·1	13·66	13·90[73,75]	+0·24	6·99	4·92	0·8	13·22	13·76[43]	+0·54	13·60	+0·23
CH_4	5·34	7·06	7·2	13·78	13·42	-0·36	2·31	5·51	4·8	13·20	13·49	+0·29	12·78	-0·68
Primary C-H bonds														
C_2H_6	3·86	5·50	9·0	13·53	13·12	-0·41	1·46	3·73	6·1	12·90	12·90	0·00	13·18	-0·10
C_3H_8	3·08	4·30	10·0	13·30	-	-	1·07	2·66	6·6	12·69	12·64	-0·05	13·23	+0·25
$n\text{-}C_4H_{10}$	2·58	4·10	10·7	13·30	-	-	0·84	2·33	6·9	12·62	12·59	-0·03	13·15	+0·20
$isoC_4H_{10}$	2·58	3·70	10·7	13·23	-	-	0·84	2·05	6·9	12·57	12·61	+0·04	13·11	+0·24
$neoC_5H_{12}$	2·22	3·34	11·3	13·20	13·17	+0·03	0·68	1·70	7·1	12·52	12·58	+0·06	13·15	+0·31
Secondary C-H bonds														
$cycloC_3H_6$	-	-	-	-	-	-	1·11	3·13	6·4	12·76	12·59	-0·17	12·95	-0·16
C_3H_8	3·08	4·90	9·0	13·23	13·41	+0·18	1·07	2·88	6·6	12·74	12·71	-0·03	13·56	+0·52
$n\text{-}C_4H_{10}$	2·58	4·05	10·5	13·26	13·62	+0·36	0·84	2·33	6·7	12·59	12·67	+0·08	13·34	+0·50
Tertiary C-H bond														
$isoC_4H_{10}$	2·58	3·6	10·5	13·18	13·30	+0·12	0·84	1·99	7·1	12·61	12·76	+0·15	13·23	+0·41
Halides														
CH_3Cl	2·83	6·61	10·3	13·82	13·14	-0·68	-	-	-	-	-	-	13·52[42]	-0·29
CH_3Br	1·83	6·90	11·6	13·95	13·25[84]	-0·70	-	-	-	-	-	-		

Entropies are in cal.$mole^{-1}deg^{-1}$ and A factors in log $mole^{-1}cm^3sec^{-1}$.

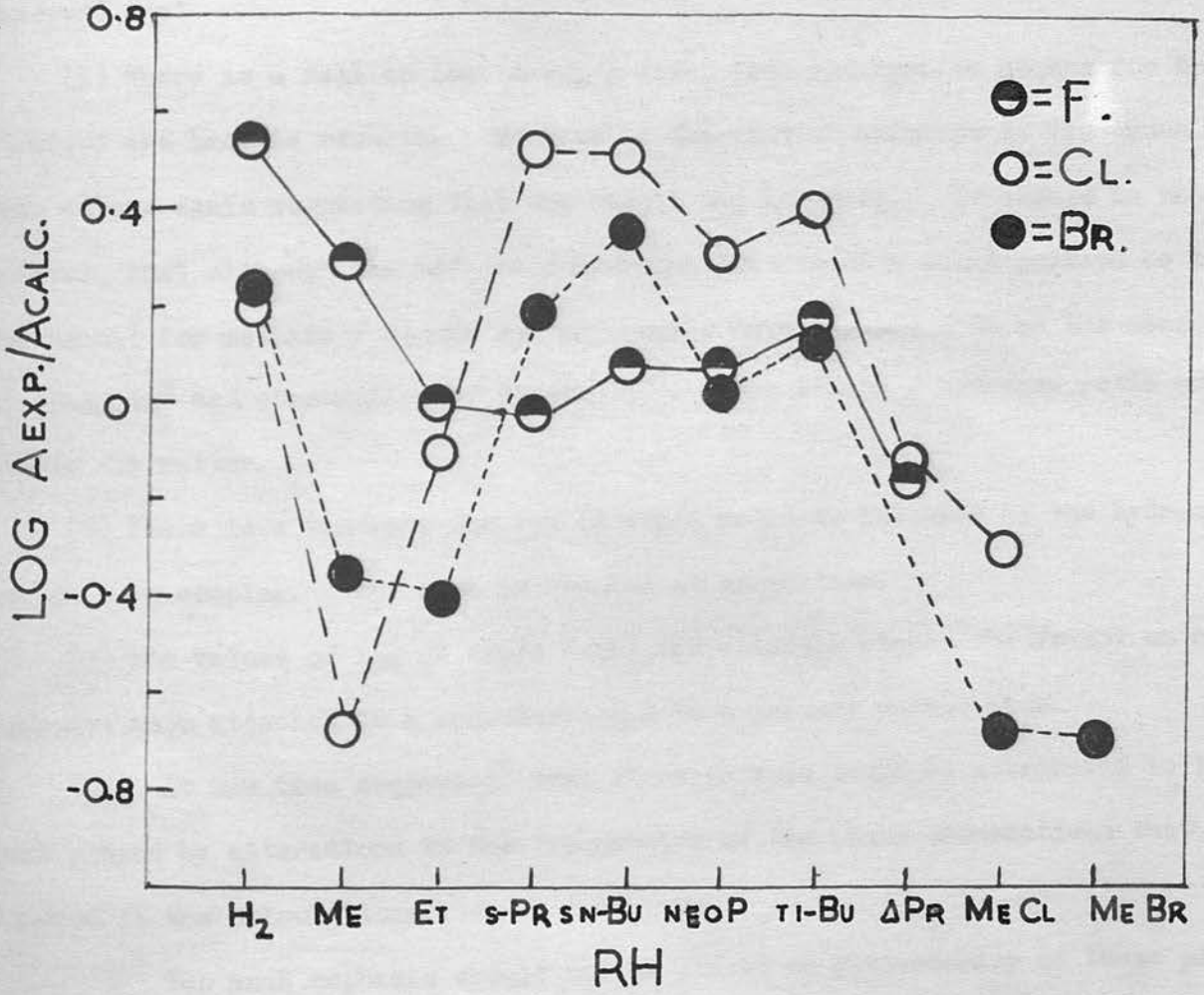

0·8
0·4
0
-0·4
-0·8
LOG AEXP./ACALC.
●=F.
○=CL.
●=BR.
H2
ME
ET
S-PR
SN-BU
NEOP
TI-BU
ΔPR
ME CL
ME BR
RH

FIG.9.1.

carbon and position attack is best seen graphically (Fig. 9·1). With the marked exception of the chlorine-methane point, the plots have the same general shape, the breaks in the lines occurring at the same places. Because of the slight uncertainties in the absolute results for chlorine and fluorine the position of their plots may be out by a constant factor on the y-axis. Notable features observed are:

(1) There is a fall in log (A exp/A calc) from hydrogen to ethane for the fluorine and bromine results. Methane in the case of chlorine is very much lower than ethane again suggesting that the result may be wrong. It should be noted, however, that although the methane / hydrogen chlorination could perhaps be in error, the result for methane / ethane was thoroughly investigated both by the measurement of products[2] and consumption of reactants[41]. The ethane / hydrogen ratio would settle the matter.

(2) There is a tendency for log (A exp/A calc) to increase as the hydrocarbons become more complex. The rise is checked at neopentane.

(3) The values of log (A exp/A calc) are slightly higher for attack on a hydrogen atom attached to a secondary than to a primary carbon atom.

It has been suggested[2] that these factors could be attributed to the part played by alterations in the frequencies of the chain deformations that were ignored in the calculations.

Too much emphasis should not be placed on the accuracy of these plots since many of the slight changes in log (A exp/A calc) could be due to experimental error. It is true to say, however, that the parallelism for the three halogens is more marked than could normally be expected, indicating the method of calculation from the transition-state theory is good. Indeed, the agreement of the calculated and experimental values is so good that it is doubtful if any legitimate adjustments could be made to the method of calculation to equate the two sets of values.

Table 9.6. Experimental Activation Energies for Fluorine, Bromine and Chlorine Atom Hydrogen Abstraction Reactions

Bond Type RH	E_2 kcal.mole^{-1} Fluorine	Bromine	Chlorine[2]
H_2	1.71[43]	18.5[73,81]	5.50
CH_4	1.21	18.25	3.85
Primary C-H bonds			
C_2H_6	0.28	13.40 ± 0.09	1.04
C_3H_8	0	-	1.00
$n\text{-}C_4H_{10}$	0	-	0.79
$IsoC_4H_{10}$	0	-	0.82
$NeoC_5H_{12}$	0	14.29 ± 0.13	0.92
Secondary C-H bonds			
$CycloC_3H_6$	0	-	4.14
C_3H_8	0	10.15 ± 0.14	0.68
$n\text{-}C_4H_{10}$	0	10.23 ± 0.23	0.27
Tertiary C-H bonds			
$IsoC_4H_{10}$	0	7.51 ± 0.20	0.02
Halides			
CH_3Cl	-	14.45 ± 0.16	3.10^{42}
CH_3Br	-	16.05[84]	-

9·3. Activation Energies for the Hydrogen Abstraction Reaction.

Absolute activation energies for bromine (Table 9·6) were obtained from the experimental differences listed in Table 9·2 using the absolute value E_2 = 16·05 kcal mole^{-1} obtained by Kistiakowsky and Van Artsdalen[84] for bromine abstraction from methyl bromide. In order to obtain approximate absolute values of E_2 (Table 9·6) from the experimental activation energy differences for fluorination listed in Table 9·3, it has been assumed that the reaction of a fluorine atom with a hydrogen in one of the higher hydrocarbons requires no activation energy. The indirect evidence for this assumption is that there is no difference between the activation energies for the different hydrogen types. Furthermore, the corresponding activation energies for chlorination are small and it is not unreasonable to expect those for fluorinations to be even smaller. The errors involved should not be large.

An examination of Table 9·6 shows that the activation energies for fluorine are small, methane and hydrogen only having appreciable values. The higher hydrocarbons probably do have activation energies of the order of a few tens of calories and small differences may exist up the series. However their detection was beyond the accuracy of the method and the results did not merit a least squares' treatment.

The activation energies for the brominations are of the order expected for hydrogen abstraction with methane > primary > secondary > tertiary. The value for neopentane is perhaps a little high but still lies within experimental error of most work for other radicals. The methyl halides lie between methane and ethane, methyl chloride having ~4 kcal less and methyl bromide ~2 kcal less than methane. Unfortunately insufficient results are available for a legitimate comparison of bromine with chlorine. It is evident that the activation energies for bromine are very much higher than for chlorine which are higher than for fluorine. The differences

between the bromine and chlorine results are much greater than between the chlorine and fluorine values. The divergences, where results are available, appear to increase in the order tertiary < secondary < primary < methane generally. They may also increase with chain length and chain branching.

The features of the chlorinations were:

(1) The activation energy for attack on the primary position decreased on ascending the alkane series.

(2) While increasing chain length led to lower values, branching of the chain led to higher results.

(3) The activation energies increased in the same order as the brominations, the difference between primary and secondary increasing on ascending the series. Cyclopropane had an abnormally high activation energy which was attributed to the reaction being unfavoured because of the additional I strain during the formation of the activated complex. No such abnormal activation energy occurred with fluorination (provided the pressure was high). The A factor, on the other hand, was high. The chlorine value for the isobutane activation energy may be low.

Calculation of Activation Energies:- Calculation of accurate activation energy values has achieved little success except for the simplest cases, not because of the absence of a basic theory, but because of the mathematical labour involved. No attempt will be made to give the theories here. Calculations for reactions of the type,

$$X + YZ = XY + Z \qquad (1)$$

have achieved some success with the aid of simplifications. The semi-empirical method of Eyring and Polanyi, an extension of the London theory, has been the most generally used[143]. The calculated results for hydrogen atom attack on the halogens and hydrogen halides tend to be higher than the experimental values[131]. The approach of Evans and Polanyi[150,143] based on potential energy profiles gives some

understanding of the factors controlling the activation energy for reactions of type (1) where X, Y and Z are atoms or radicals. The value of the activation energy is controlled by five factors:

(1) The strength of the bond broken Y-Z

(2) The repulsion energy between X and YZ.

(3) The repulsion energy between XY and Z

(4) The strength of the bond formed X-Y

(5) Resonance in the activated complex.

Positive increments in (1), (2) and (3) should increase the activation energy for the reaction whereas an increase in (4) and (5) should decrease it.

It is possible to construct a potential energy profile, neglecting the resonance energy, for a reaction from potential energy curves of systems having the bond assignments of YZ and XY. The potential energy for YZ is given by,

Potential energy = $R_{XYZ} + B_{YZ}$

where R_{XYZ} and R_{YZ} are factors (2) and (1) respectively given before. Similarly the energy for XY is given by (3) and (4). Fig. 9·2 shows the construction of such curves for fluorine, chlorine, bromine and iodine hydrogen abstraction from methane and the tertiary in isobutane. This was only a qualitative attempt to calculate activation energies and the repulsion terms R have been ignored. While the energy of repulsion is small for the reactants Na + RCl, it can be appreciable for the reactions considered here. However the repulsion effects of the reactants and products partly cancel (both curves are raised) and qualitative information can be obtained without their inclusion. The potential energy has been calculated from the bond energy term using the Morse equation[151]

$$U = \frac{D_e\left[1-e^{-\beta(r-r_e)}\right]^2}{r-r_e}$$

where U is the potential energy, $D_e(cm^{-1})$ is the dissociation energy of the bond

referred to the minimum; $r-r_e$ is the stretching or compressing distance from the equilibrium interatomic distance r_e for the normal molecule XY or YZ. β is given by:

$$\beta = 1{\cdot}2177\, \nu_e \sqrt{\frac{\mu_A}{D_e}}$$

where μ_A is the reduced mass in atomic weight units. D_e may be obtained to a good approximation from,

$$D_e \simeq D_o + \tfrac{1}{2} \nu_e$$

where $\nu_e(cm^{-1})$ is the frequency for infinitesimal amplitude and $\frac{1}{2} W_e$ corresponds approximately to the zero point energy. D_o is the heat of dissociation of the molecule.

In summary the values used for Fig. 9·2 were:

Bond	D_e cm^{-1}	β
C-H in methane	37,560	1·90
C-H in isobutane	32,720	1·96
H-F	49,069	2·23
H-Cl	37,195	1·87
H-Br	31,545	1·81
H-I	25,805	1·75

A reasonable series of values for $r-r_e$ (r^1 in Fig. 9·2) was chosen so that the movement of the hydrogen between R and X(kept at constant distance) could be followed, drawing the stretching and compression curves of R···H and H···X respectively. The curves are placed correctly relative to each other by obtaining the correct value for the heat change in the reaction (the positive distance between virtually the minima of the two sets of curves for a given reaction is the exothermicity). The endothermicity of iodine atom abstraction and the exothermicity of fluorine atom abstraction is apparent. The height above the minima on this scale at which the two curves cross represents the activation energy. The dotted lines are an attempt to show the effect of resonance in the complexes.

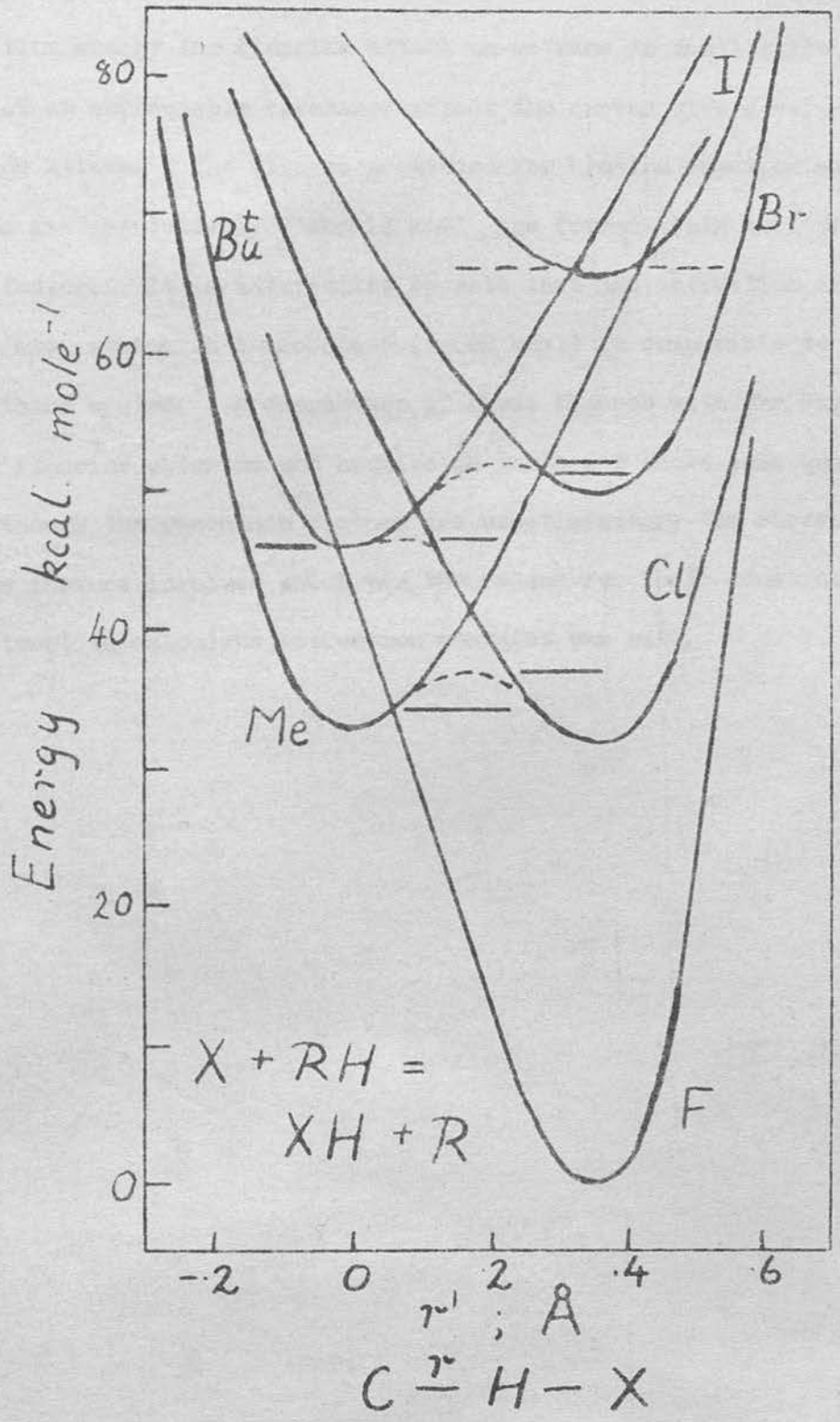

80
60
40
20
0
Energy kcal. mole⁻¹
I
Br
Bu^t
Cl
Me
F
X + RH =
XH + R
-.2
0
.2
.4
.6
r' ; Å
C r H – X

FIG. 9.2.

It is seen that zero activation energy is predicted for fluorine attack on the tertiary hydrogen in isobutane and virtually zero for similar chlorine attack. The activation energy for fluorine attack on methane is small while, with the inclusion of an appreciable resonance effect, the curves give a value of ~ 4 kcal for chlorine attack. The figures predicted for bromine reaction with t-isobutane and methane are respectively 7 and 18 kcal, the former again includes an appreciable resonance factor. It is interesting to note that the activation energy predicted for iodine atom attack on t-isobutane (~ 20 kcal) is comparable to that for the bromine-methane system. A comparison of these figures with the experimental values for fluorine, chlorine and bromine in Table 9·6 shows some qualitative agreement. Although the resonance factors are unsatisfactory the curves do give some idea of the factors involved, which was the reason for their construction. No serious attempt to calculate activation energies was made.

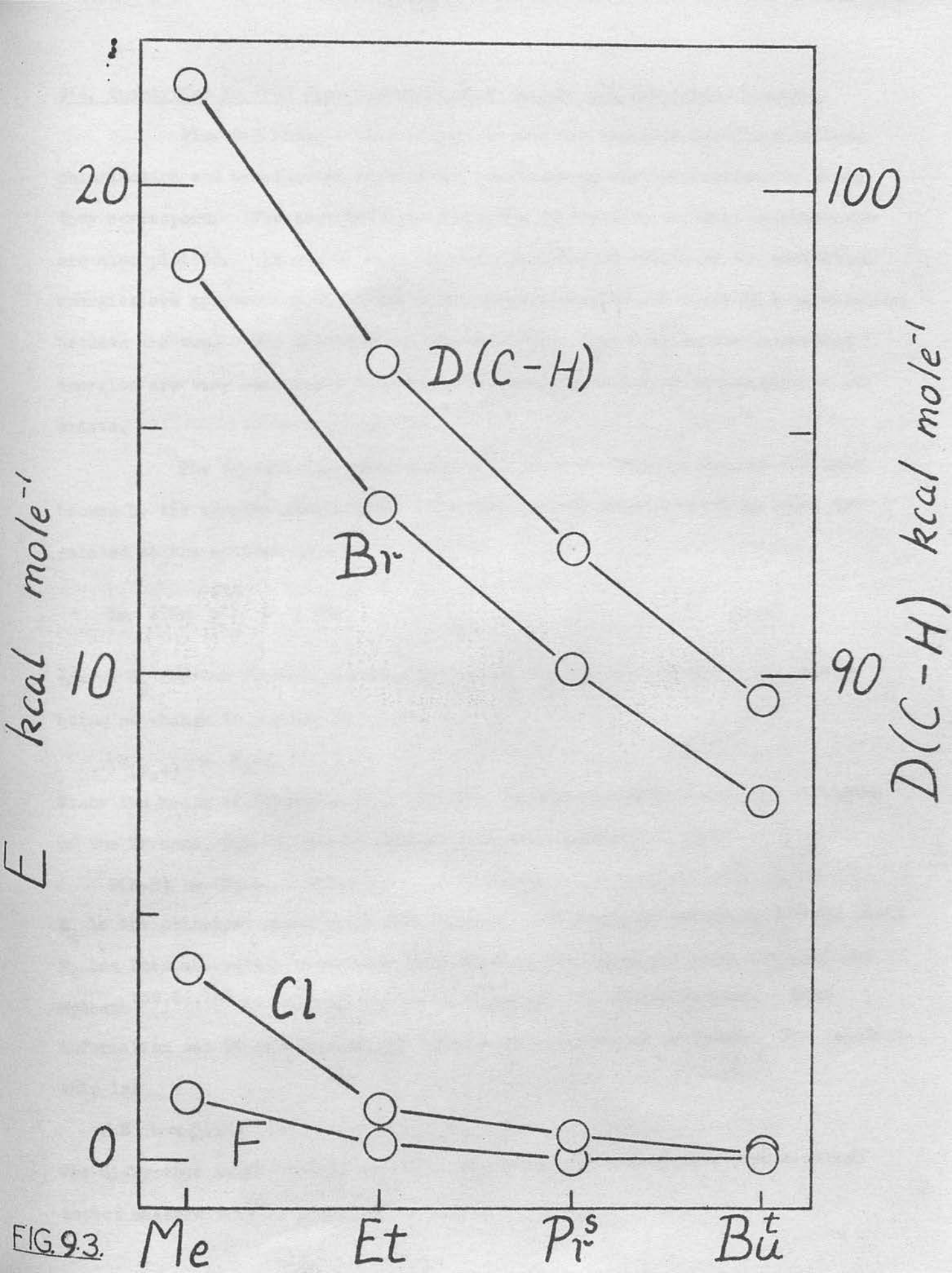

20
10
0
E kcal mole⁻¹
100
90
D(C-H) kcal mole⁻¹
D(C-H)
Br
Cl
F
Me
Et
Pr^s
Bu^t

FIG. 9.3.

9·4. Quantities Derived from Experimental A Factors and Activation Energies.

Fig. 9·3 shows a plot of some activation energies for fluorination, chlorination and bromination against the positions in the hydrocarbons to which they correspond. The accepted bond strengths appropriate to these hydrocarbons are also plotted. It can be seen that for bromination values of the activation energies are approaching the order of the bond strengths and there is a parallelism between the two. For chlorination and especially fluorination the activation energies are very much lower than the bond strengths and very little parallelism exists.

The bromination results can lead to bond strengths for the C-H bond broken by the bromine atom attack. The heat of the overall reaction (2,4) is related to the activation

$$Br\cdot + RH \underset{(4)}{\overset{(2)}{\rightleftharpoons}} R\cdot + HBr \qquad (2,4)$$

energy E_2 for the forward reaction (2) and E_4 for the back reaction (4), there being no change in volume, by

$$\Delta H_{(2,4)} = E_2 - E_4$$

Since the heats of formation of $H\cdot$, $Br\cdot$ and HBr are accurately known, the strengths of the RH bond, D(R-H), can be derived from the equation,

$$D(R-H) = E_2 - E_4 + D(H-Br).$$

E_4 is the principal uncertainty and reliable bond strengths cannot be derived until E_4 has been accurately determined from experiment. Only the bond strengths for methane[152,84,153] is reliable of the previous kinetic determinations. Some information can be obtained if the Polanyi relationship is accepted. The relationship is:

$$\Delta E = \alpha \Delta(\Delta H)$$

The difference in ΔH between the cases of methane and t-isobutane from electron impact measurements[154] is given by,

$D(Me-H)-D(t.Bu-H) = 12{\cdot}5$ kcal.

From the bromine experiments,

$E_2(Me-H)-E_2(t.Bu-H) = 10{\cdot}74$ kcal.

The electron impact results may be in error by 2 or 3 kcal. Hence α lies between 0·72 and 1 (it cannot be greater than 1)[48], with a most probable value of 0·86. This value has been used to obtain the bond strength results listed in Table 9·7 from the experimental E_2's and $D(CH_3-H)$. The resulting E_4 values are also tabulated as well as the currently accepted values of bond strengths which compare well with our results.

The Polanyi relationship, however, has not been clearly established for any series of reactions, largely because of inadequate knowledge of bond strengths. It might be expected to hold when α is high as in this case. The preliminary work reported on the photolysis of ketone-hydrogen bromide-iodine mixtures was an attempt to prove the existence of the Polanyi relationship. It was found that for the reactions,

$$C_2H_5\cdot + HBr \longrightarrow C_2H_6 + Br\cdot \qquad (4)$$

and

$$C_2H_5\cdot + I_2 \longrightarrow C_2H_5I + I\cdot \qquad (6)$$

$E_4-E_6 = 2{\cdot}1$ kcal.

This gives a minimum value of $E_4 = 2{\cdot}1$ kcal since, as we saw before, E_6 may have a small positive value. The value predicted from the Polanyi relationship for E_4 was 2·5 kcal. This is good evidence in support of the relationship. Further work on say isobutyl radicals should either confirm or disprove the validity of the relationship. If it is disproved, in order to obtain true bond strengths all the individual activation energies for radical attack on HBr will have to be determined somehow.

Also listed in Table 9·7 are values of $\log A_4$ obtained from A_2 and the relationship,

$$R\ln(A_2/A_4) = \Delta S_{2,4}.$$

Table 9·7. D(R-H) for Alkanes and Arrhenius Parameters for the Reactions (4) of Alkyl Radicals with Hydrogen Bromide.

Alkyl	S^{146} cal.mole^{-1}deg^{-1}	E_2 kcal.mole^{-1}	E_4 kcal.mole^{-1}	$\log A_4$ mole^{-1}cm^{3}sec^{-1}	D(R-H) kcal.mole^{-1}(25°C) This work	Ref.155
Methyl	47·2	18·3	1·8	12·2	102·5	102.5
Ethyl	58·5	13·4	(2·5)	11·9	96·9	97
Neopentyl	78·2	14·3	(2·4)	12·0	97·9	96·5
Isopropyl	65·9	10·2	(3·1)	12·2	93·1	95
s-Butyl	76·8	10·2	(3·1)	12·4	93·2	-
t-Butyl	70·4	7·6	(3·6)	12·1	90·0	90·5

The entropies used for the radicals[146] are shown in column 2. of Table 9·7.

The activation energy for (5) can also be estimated from the relationship (7);

$$Br\cdot + RBr \longrightarrow Br_2 + R\cdot \qquad (5)$$

$$\Delta H_s = E_2-(E_4-E_3)-E_5 \qquad (7)$$

where E_3 is for the reaction,

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (3)$$

and ΔH_s is the heat change for the overall reaction (8)

$$Br_2 + RH \rightleftharpoons RBr + HBr \qquad (8)$$

Calculations of this type have been carried out by Benson and Buss[97] (the references in their table are wrongly numbered). However only in the cases of methane, hydrogen (and ethane) have any semi-reliable experimental values for E_4-E_3 been obtained. The results are shown in Table 9·8.

Table 9·8.

Hydrocarbon, RH	E_2	E_4-E_3	ΔH_s[97]	E_5
H_2	18·5[73,81]	0[73,81]	-24·5	43·0
CH_4	18·25	2·0[84]	- 6·5	22·8
C_2H_6	13·40	0[90]	-11·0	24·4

All units are keal mole^{-1}

It could be argued that since the variation in the E_4 values is small (from our work) and the variation in the R-Br bond strengths is less than those in the R-H cases, little variation should occur in E_3 values. However calculations of E_5 based on this assumption have no experimental guarantee of accuracy and were not thought to be worth while. The accuracy is also limited by uncertainties in ΔH_s.

Carbon-carbon bond strengths can also be calculated from a knowledge of the heats of formation of the alkyl radicals obtained from the equation:

$$\Delta Hf(R\cdot) = \Delta Hf(R\text{-}H) - \Delta Hf(H\cdot) + D(R\text{-}H)$$

where ΔHf is the heat of formation at 25°C. The derivation of D(C-C) is best seen from an example:

$$D(CH_3\text{-}C_2H_5) = \Delta Hf(CH_3) + \Delta Hf(C_2H_5) - \Delta Hf(C_3H_8)$$

$$= 32{\cdot}5 + 24{\cdot}6 + 24{\cdot}8 = 81{\cdot}9 \text{ kcal mole}^{-1}$$

A few of the possible results are shown in Table 9·9.

Table 9·9. Heats of Formation of Radicals and D(C-C) Values.

Alkane	ΔHf[156] (25° C)	Radical	ΔHf (25° C)	C-C Bond	D(C-C) (25° C)
		H	52·09[157]		
CH_4	-17·89	CH_3	32·5	$CH_3\text{-}CH_3$	85·2
C_2H_6	-20·24	C_2H_5	24·6	$C_2H_5\text{-}CH_3$	81·9
C_3H_8	-24·82	iso-C_3H_7	16·2	$C_2H_5\text{-}C_2H_5$	79·4
n-C_4H_{10}	-30·15	s-C_4H_9	11·0	iso-$C_3H_7\text{-}C_2H_5$	80·9
iso-C_4H_{10}	-32·15	t-C_4H_9	5·8	t-$C_4H_9\text{-}CH_3$	78·0
neoC_4H_{10}	-39.67	neoC_5H_{11}	6.1		

All units are kcal mole^{-1}

9·5. Factors Affecting Rates.

The results for fluorine, chlorine and bromine have been co-ordinated in Table 9·10. It can be seen that for fluorine the relative rate at the different types of hydrogen is controlled by the size of the A factor even in the case of ethane which has a small activation energy. With methane and especially hydrogen it is the activation energy that is important, however. Fluorine is a rather exceptional case since with bromine and chlorine, as with most other radicals undergoing metathetical reaction, the controlling factor is the activation energy. Any attempt to estimate the rate of a reaction reduces to a prediction of the activation energy of that reaction. The relative rate constants for attack of the halogens at primary, secondary and tertiary bonds are listed in Table 9·11 along with the results for the hydrogen abstraction reactions of other radicals in the gas phase. The reactivity of the radical X has been correlated with the activation energy for its attack on ethane. Fluorine is the most and bromine the least reactive of the radicals quoted. Some of the factors controlling the activation energy have been discussed in Chapter 9·3. The subject has been discussed else-where[38,48,161,162] and no attempt will be made to generalise here. Factors affecting the ease of approach of the attacking radical to the substrate and the availability of electrons to form a bond and to remain there must be considered. Finally the kinetic parameters from the present and previous hydrogen abstraction experiments with bromine atoms have been summarised in Table 9·12.

Table 9·10. Halogen Absolute Activation Energies, A Factors Rate Constants

Bond Type RH	← Bromine → E_2 kcal.mole^{-1}	$\log A_2$ mole^{-1}cm^{3}sec^{-1}	k_2(25° C)	$\frac{k_{RH}}{k_{Et}}$(25° C)
H_2	18·5[73,81]	13·9	2·19	1·10 x 10^{-3}
CH_4	18·25	13·42	1·05	0·53 x 10^{-3}
Primary C-H bonds				
C_2H_6	13·40 ± 0·09	13·12 ± 0·04	2·00 x 10^3	1·00
C_3H_8	-	-	-	-
n-C_4H_{10}	-	-	-	-
IsoC_4H_{10}	-	-	-	-
NeoC_5H_{12}	14·29 ± 0·13	13·17 ± 0·06	5·01 x 10^2	2·50 x 10^{-1}
Secondary C-H bonds				
CycloC_3H_6	-	-	-	-
C_3H_8	10·15 ± 0·14	13·41 ± 0·07	9·33 x 10^5	4·67 x 10^2
n-C_4H_{10}	10·23 ± 0·23	13·62 ± 0·14	1·32 x 10^6	0·66 x 10^3
Tertiary C-H bond				
IsoC_4H_{10}	7·51 ± 0·20	13·30 ± 0·11	6·24 x 10^7	3·12 x 10^4
Halides				
CH_3Cl	14·45 ± 0·16	13·14 ± 0·06	3·55 x 10^2	1·78 x 10^{-1}
CH_3Br	16·05[84]	13·25	3·02 x 10	1·51 x 10^{-2}

Table[158] 9·11.

Radical D(R-H)	Temp° C 25	Rel. Rate Constants Me. 102·5	Prim. 96·9	Sec. 93·2	Tert. 90·0	E_2(EtH)	D(XH)	Ref.
Radical X								
F	25	0·08	1	1·2	1·4	0·3	134	this work
Cl	250	0·03	1	3	3	1·0	103	2
HO_2,RO_2 or OH	350	0·07	1	4	11	-	-	159
CF_3	182	0·08	1	6	36	7·5	102	160
CH_3O	250	-	1	8	26	-	102	158
CH_3	182	0.04	1	7	50	11	102.5	48
Br	98	0·002	1	250	6300	13·4	86	this work

All energies are in keal. $mole^{-1}$

Table 9.12. Summary of Arrhenius Paramaters for Reactions of Bromine - Organic Systems (p.83)

RH	E_2	$\log A_2$	$\log k_2$ (100° C)	E_4-E_3	E_4	A_4/A_3	Ref.
H_2	18·5	14·2	3·36	0	~0	$\frac{1}{10}$, $\frac{1}{8.4}$	73,75,81
	17·7	13·8	3·43	-	-	-	76,81
	17·6	13·8	3·48	0	~0	1/10	77,81
	17·5	13·7	3·28	-	-	-	84
	17·8	13·7	3·27	assumed 0	1.6	$10^{13\cdot7}/10^{14\cdot4}$	86,88,73,75
	18·8	14·1	3·09	"	2·2	$10^{13\cdot6}/10^{14\cdot6}$	89
	18·3	14·0	3·32	-	-	-	87
	-	-	-	-	0 ± 1800	-	134
	-	-	-	-	< 3	-	133
	-	-	-	-	1	-	130
	18·2 ± 0·6	-	-	-	1·5 ± 0·6	-	this work
D_2	19.9	13·9	2.23	-	-	-	76
CH_4	18.25	13·8	3·07	2	1·5 ± 1	0·2	84,132
	18.25	14·02	3·32	-	1·8	$10^{12\cdot2}/10^{12\cdot9}$	this work
C_2H_6	13.40	13·90	6·05	-	2·5	$10^{11\cdot9}/10^{12\cdot1}$	this work
	13.9	-	-	0	< 2	0·6	90
(sec)C_3H_8	10.15	13·71	7·76	-	3·1	$10^{12\cdot2}/?$	this work
(sec)n-C_4H_{10}	10.23	13·22	7.23	-	3·1	$10^{12\cdot4}/?$	"
(tert)IsoC_4H_{10}	7.51	13·30	8·90	-	3·6	$10^{12\cdot1}/?$	"
IsoC_4H_{10}	(11·7)	(17·6)	(10·7)	(8·0)	(8·0)	$(10^{5\cdot1}/1)$	93
$NeoC_5H_{12}$	14·29	14·24	5·87	-	2·4	$10^{12\cdot0}/?$	this work
	(18·1)	(17·0)	(6·3)	(9·9)	(9·9)	$(10^{5\cdot8}/1)$	91
$C_6H_5CH_3$	(7·6)	(13·5)	(9·1)	(5·0)	(5·0)	$(10^{3\cdot0}/1)$	92
CH_3Br	16.05	13.73	4·33	-	-	-	84
CH_3Cl	14·45	13·62	5·15	-	-	-	this work
$CHCl_3$	10	-	-	0	6·7	(0·14)	99
	9·3	12·3	6·8	0	≤ 7	0·04	101
CCl_3CHO	<8,8 ± 3	-	-	-	-	-	103,104
C_6H_6	~7	-	-	-	-	-	105
$\alpha C_{10}H_8$	0-5	-	-	-	-	-	108
C_6H_{12}	8.5	-	-	-	-	-	115

E's in keal $mole^{-1}$ A's and k's in $mole^{-1}$ cm^3 sec^{-1}
Bracketed values have been shown to be of doubtful validity. Note A factors and rate constants are all per molecule here.

9·6. Future Work.

The usefulness of the competitive method has been shown by this work. Of course the method is not new, for all kinetic measurements involve competition against some standard. Just as one is careful about choosing a reliable time standard, so one should choose a well established reaction for the method used here. The measurement of absolute rates are invaluable in this respect.

The reaction of fluorine atoms with fluoroform should be sufficiently slow to be measurable if the experimental difficulties could be surmounted. reactions of iodine atoms, too, should not be ignored. Using the competitive method the reactivities of substituted hydrocarbons to fluorine and the reactions of ketones and other compounds with fluorine and bromine should be interesting. Fluorine atom attack on halogenated alkanes should be of especial interest. Addition to unsaturates may prove difficult with bromine but should lead to quick, accurate results with fluorine. The competitive method could be applied also to other well established kinetic systems.

A knowledge of the activation energies of reactions of the type

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (3)$$

would be useful. Unfortunately radical competition with bromine and iodine would be complicated by iodine bromide formation. Some information could be obtained by using the alkanes as a photolytic source of radicals in the presence of DBr and Br_2 to compete for the radicals.

It is proposed to refine the method described in the text for obtaining activation energies of reactions of the type,

$$R\cdot + HBr \longrightarrow RH + Br\cdot \qquad (4)$$

The iodides formed will be passed over KOH or some other agent to remove HI and the resulting olefins measured. This should avoid errors caused by olefin formation in the reaction vessel which was indicated in the case of isopropyl iodide and which

probably will occur with t-butyl iodide. In order to obtain really accurate bond strengths a knowledge of the activation energy for

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (11)$$

is required. It is proposed to photolyse ketones in the presence of iodine and measure dimer alkanes arising from the competing reaction (10)

$$R\cdot + R\cdot \longrightarrow RR \qquad (10)$$

The use of the Lovelock detector in conjunction with the detector used here will be necessary. Incidentally more use should be made of such a set-up for kinetic measurements, e.g. the combination of the Janak system with the method of analysis used in this work might be useful.

The ketone-iodine system has other possibilities, e.g. competition of the reactions,

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO \xrightarrow{I_2} CH_3I$$

with $CH_3CO\cdot + I_2 \longrightarrow CH_3COI + I\cdot \qquad (12)$

would give the difference in activation energy between the breaking of the C-CO bond and the small activation energy for reaction (12). In order to do this however a knowledge is required of the amount of the initial photolytic split from the reaction,

$$C_2H_5COCH_3 + h\nu \longrightarrow CH_3\cdot + CO + C_2H_5\cdot \qquad (20)$$

However by adding sufficient iodine to the system reaction (12) could occur exclusively with acetyl radicals. Any methyl iodide formed should arise from methyl radicals formed in the initial split which could then be estimated. Carefully controlled illumination of the longer wavelengths might be required for this system.

A knowledge of E_{11} leads to other possiblities in the iodine series. Consider the reactions,

$$CH_3\cdot + HI \underset{k_{15}}{\overset{k_{14}}{\rightleftharpoons}} CH_4 + I\cdot,$$

$$CH_3 + I_2 \underset{k_{16}}{\overset{k_{11}}{\rightleftharpoons}} CH_3I + I\cdot$$

k_{11}/k_{14} and consequently $E_{14}-E_{11}$ and E_{14} are known[135]. $E_{14}-E_{15}$ can be derived thermochemically and so E_{15}, the activation energy for iodine atom hydrogen abstraction, found. A consideration of isobutane in such a system should also be interesting.

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APPENDIX.

The fluorination work has been published. The paper is incorporated in the back cover. Errors in log A exp in Table 2 for the methane and hydrogen fluorine results have been corrected in this thesis. The energy units in Table 1 of the paper have also had to be corrected here.

A preliminary note on the bromine hydrogen abstraction work is also included. A more detailed paper is being submitted for publication.